

STUDY OF TRANSPORT AND INTERMOLECULAR INTERACTIONS IN COMPRESSED SUPERCRITICAL FLUIDS

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General overview of several studies of transport and intermolecular interactions in compressed supercritical fluids will be presented. The unique aspects of the instrumentation used in these studies will also be emphasized. First, the results of NMR studies of self-diffusion in supercritical ethylene and toluene will be discussed. These experiments are using the fixed field gradient NMR spin-echo technique. Second, the novel NMR technique for the determination of solubility of solids in supercritical fluids will be described. Third, the promising potential of laser scattering experiments investigating interaction induced spectra will be illustrated on several specific studies of depolarized Rayleigh scattering. The interaction induced spectra offer valuable information about intermolecular interactions in supercritical fluids.

Introduction

Research on the properties of supercritical fluids and supercritical fluid mixtures has become very important in recent years due to the great promise of supercritical fluid extraction techniques. These techniques and their applications have been reviewed by several authors (1-4). There are many advantages of using supercritical fluid extraction over conventional extraction techniques. Many low volatility molecular solids show greatly enhanced solubilities in supercritical dense fluids. Solvent recovery is easily accomplished by manipulating the density, and therefore the solvating power, of the supercritical fluid to precipitate the solid. In addition, although the densities of the supercritical fluids are comparable to liquid densities, the viscosities are generally an order of magnitude smaller, and diffusivities an order of magnitude larger than liquids. A more efficient separation can therefore be achieved.

Unfortunately, there is a lack of fundamental data on transport and relaxation in model fluids at supercritical conditions. Not surprisingly, there is a corresponding lack of theoretical models to explain the dynamics of supercritical fluids on a molecular level, particularly at the intermediate densities.

The main purpose of our work is the improvement of molecular level understanding of solute-solvent interactions under supercritical conditions. Unique nuclear magnetic resonance (5) and laser scattering techniques (6) are employed to obtain new information about dynamics of molecules in supercritical fluids at high pressures.

The main results of several of our studies will be discussed. First, the results of NMR studies of self-diffusion in supercritical ethylene (7) and toluene (8) will be discussed. These experiments are using the fixed field gradient NMR spin-echo technique. Second, the novel NMR technique (9) for the determination of solubility of solids in supercritical fluids will be described. Third, the promising potential of laser scattering experiments investigating interaction induced spectra (6) will be illustrated on several specific studies of depolarized Rayleigh scattering.

Experimental

The self-diffusion coefficients in supercritical ethylene were measured using the pulsed NMR spectrometer described elsewhere (10), automated for the measurement of diffusion coefficients by the Hahn spin echo method (11). The measurements were made at the proton resonance frequency of 60 MHz using a 14.2 kG electromagnet.

The pressure was generated using the gas compression system described previously (12). A Heise-Bourdon pressure gauge was installed between the compression system and the high pressure vessel to supplement the 30,000 psi pressure transducer. The oxygen scavenger system was bypassed as the amount of oxygen in the ethylene was below the minimum detection level (10 ppm) of the oxygen analyzer (Beckman Instruments, Inc.). In order to depress the extremely long T_1 values of pure ethylene (13) at the experimental conditions studied, small quantities (< 1000 ppm) of oxygen were mixed with the ethylene before measurement of the diffusion coefficient. The addition of oxygen brought the T_1 values down to 2-3 sec, but should not affect the value of the diffusion coefficient. The shorter T_1 values allowed a much shorter measurement time.

The self-diffusion coefficients in supercritical toluene- d_6 were measured at the deuterium resonance frequency of 9.21 MHz, using a 14.1 kG electromagnet with a wide gap (3.8") to accommodate the high pressure vessel. The pulsed NMR spectrometer and receiver system were described in detail elsewhere (10). The argon pressurized high pressure, high temperature NMR probe (14) was used previously for studies of relaxation (15) and diffusion (16) in compressed supercritical water. It consists of two high pressure vessels: the primary vessel, containing an internal furnace, two thermocouples and the RF coil and sample, and the secondary vessel, containing the stainless steel sample bellows. Quartz sample cells were used rather than ceramic cells, as corrosion is not a problem. The RF coil was constructed by winding 14 1/2 turns of 22 gauge nichrome (Chromel A) wire. The coil was silver soldered to nichrome conductor coaxial high pressure leads. The tuning circuit consisted of a six foot impedance transforming coaxial cable terminated with a tapped-parallel capacitor box with both fixed and variable capacitors totalling 70 pF in series and 10 pF in parallel. The observed signal peak to rms noise ratio in liquid toluene- d_6 (30°C) was 60:1 after one scan.

Some experimental detail (9) on the experimental NMR setup for the measurement of solubilities of organic solids in supercritical fluids will be given in the section dealing with Results and Discussion.

The description of equipment and experimental techniques for laser Rayleigh scattering experiments on supercritical fluids at high pressures were given earlier (6,17,18).

Results and Discussion

Self-Diffusion in Compressed Supercritical Ethylene

The main purpose of our work (7) was to provide transport data on dense supercritical ethylene and to analyze the data in terms of currently available theories. Ethylene was chosen for the study for a number of reasons. First, it is one of the most widely used solvents in industry due to its easily accessible critical temperature, its relatively low cost and wide availability. Highly accurate compressibility data are available (19,20,21) in the literature over a wide range of temperature and pressures. These data are necessary for a complete analysis of the transport data.

Some measurements have been made of self diffusion in pure ethylene and in ethylene-sulfur hexafluoride mixtures (22), but these measurements were made very close to the critical temperature and up to pressures of only about 100 bar. Proton spin-lattice relaxation times (T_1) of ethylene have been measured at temperatures from 0°C to 50°C and pressures up to about 2300 bar (13). The relaxation time values were 40-50 sec for much of the region studied. Several relaxation mechanisms contribute to this long relaxation time and make both the measurement and analysis of the relaxation times very difficult. For these reasons, we decided to limit our study to the measurement of the self-diffusion coefficient in supercritical ethylene.

The measurements were made as a function of density for pressures from 1 - 2000 bar and at 50°, 75°, 100° and 125°C. The temperatures chosen correspond to those for which density data (19-21) for ethylene and ethylene-CO₂ are available.

The density dependence of the ethylene self-diffusion coefficients was analyzed using the Enskog theory (23) of diffusion of hard spheres corrected for the effects of correlated motion (24). The corrected Enskog theory considers only repulsive forces between molecules, but it has proved to be in excellent agreement with experiment for the transport coefficients of supercritical dense gases such as argon, krypton, methane and carbon tetrafluoride (25). At densities less than the critical density (ρ_c), the attractive forces between the molecules become important and deviations from the theory are observed.

In previous work on supercritical fluids, Jonas et al. (26-28) measured self-diffusion, shear viscosity and angular momentum correlation times in very dense ($\rho > 2\rho_c$) supercritical fluids of simple polyatomic molecules such as SF₆, CF₄, CFC1₃ and C₄F₈. The goal of the experiments was to investigate the applicability of the rough hard sphere (RHS) model (29) at very high densities. At these high densities, the harsh, short ranged repulsive forces screen out the long range attractive forces. The RHS model accounts for the coupling between rotational and translational motion and was found to agree well with the experimental data for $\rho > 2\rho_c$. However, at the lower densities, deviations between the theory and experiment were observed for angular momentum relaxation in CF₄ (12) and mixtures of CF₄ with argon and neon (30). These deviations were attributed to the effects of attractive forces, causing the RHS model to break down. A theoretical model based on optimized cluster theory (31) was proposed (12) to account for the effects of attractive forces and was found to give a good explanation of the experimental data.

Another problem with applying the Enskog theory to explain the ethylene data is that ethylene is not spherical. Attempts to develop a theoretical description of the dynamics in fluids of non-spherical molecules have been made for many years. The model which most closely corresponds to the molecular shape of ethylene is the prolate spherocylinder. Curtiss and Muckenfuss (32) developed a kinetic theory for non-spherical molecules in the dilute gas region and applied it to the calculation of the diffusion coefficient of a spherocylinder in this region (33). They showed that diffusion in a spherocylinder fluid is faster than in a fluid composed of spheres of the same volume as the spherocylinder. In a limited molecular dynamics study (34) the values of the self-diffusion coefficient at two different densities in the intermediate region for a spherocylinder of length-to-breadth ratio equal to one were calculated. More extensive calculations have been made of the equations of state, compressibility ratios and virial coefficients for a variety of length-to-breadth ratios for spherocylinders (35-37). However, due to the lack of any complete theoretical description or molecular dynamics data for the density dependence of diffusion in a spherocylinder fluid with the ethylene length-to-breadth ratio, we used hard sphere theory to interpret our data.

Self-Diffusion in Compressed Supercritical Toluene-d₈

Our investigation was motivated by the interest in supercritical toluene as a solvent in the extraction of thermally generated coal liquids (38,39). Typically, coal is heated to temperatures between 350° and 450°C in the presence of a supercritical fluid at a pressure of 100-200 atm. As the large molecular weight components depolymerize thermally, the resulting hydrogen rich material dissolves in the supercritical solvent and is removed. Toluene is a convenient solvent to use for the extraction, as its critical temperature is 319°C, and critical pressure is 41 atm. Recent experimental studies of supercritical fluid extraction in the process of coal liquefaction investigate the basic steps involved by varying solvents, pressure and temperatures (40). The goal of our experiment was to provide fundamental data on transport in supercritical toluene-d₈. These data should help in the design and interpretation of extraction processes using supercritical toluene.

We have measured the self-diffusion coefficient in supercritical toluene-d₈ for temperatures from 300°C to 450°C ($0.97 \leq T_r \leq 1.22$) for pressures of 100, 500 and 1000 bar.

Self diffusion coefficients of deuterated toluene were measured, rather than protonated toluene in order to minimize the experimental difficulties associated with very long proton spin lattice relaxation times (T_1). Since the value of the T_1 determines the length of time between pulse sequences, a long relaxation time leads to prohibitively long measurement times. Previous measurements (41-43) of proton and deuterium relaxation times in liquid toluene have been made as a function of temperature and pressure. The relaxation is due to dipolar interactions in protonated toluene and quadrupolar interactions in toluene-d₈. Therefore, the relaxation times can be expected to increase with increasing temperature. However, the quadrupolar relaxed deuterium T_1 values are smaller than the proton T_1 values, resulting in a comparatively shorter measurement time. The self diffusion coefficients of deuterated toluene should not be significantly different from those of protonated toluene at the temperatures of the measurement and will provide an excellent estimate.

Our previous study (16) of self diffusion in compressed supercritical water compared the experimental results to the predictions of the dilute polar gas model of Monchick and Mason (44). The model, using a Stockmayer potential for the evaluation of the collision integrals and a temperature dependent hard sphere diameters, gave a good description of the temperature and pressure dependence of the diffusion. Unfortunately, a similar detailed analysis of the self diffusion of supercritical toluene is prevented by the lack of density data at supercritical conditions. Viscosities of toluene from 320°C to 470°C at constant volumes corresponding to densities from $\rho/\rho_c = 0.5$ to 1.8 have been reported (45). However, without PVT data, we cannot calculate the corresponding values of the pressure.

The diffusion data at 100 bar are compared to values obtained using various estimation schemes for the self diffusion coefficient of protonated toluene. No attempt was made to estimate coefficients at 500 and 1000 bar, as these correspond to reduced pressures ($P_r = 11.9$ and 24.7) well beyond the range of the approximative methods.

Naphthalene Solubility NMR Measurements in Supercritical Carbon Dioxide

We have completed our study of naphthalene solubilities in supercritical carbon dioxide (9). Our unique, in situ NMR method has been used to obtain solubility data for this system at 50.0, 55.0 and 58.5°C in the pressure range of 120-500 bar. Although this system had been previously investigated (46) we have defined better the solubilities near the upper critical end point of the binary mixture. And finally, we have completed our determination of the three phase solid-liquid-vapor curve of the system.

We have developed our static NMR method for the determination of solid solubilities in supercritical fluids. Using this technique we found our 55°C solubility data to agree to within 5% of that taken by Paulaitis, et al. (46), with their technique. We have since proceeded to take data along the previously uninvestigated 50.0 and 58.5°C isotherms. A number of interesting features can be noted. First, by extending the pressure range to 500 bar we were able to observe the limiting solubilities at these isotherms, an effect not before seen for this system. Secondly, the isotherms cross at about 160 bar showing the presence of the two critical end points for the naphthalene/carbon dioxide system. And finally, the 58.5°C isotherm shows a point of inflection at about 235 bar. This behavior shows the close proximity to the upper critical end point (UCEP) temperature and pressure.

The location of the UCEP is quite important to supercritical solubilities, as this critical point gives the maximum temperature at which solid-gas equilibrium exists at all pressures. We have also developed an NMR method to determine for the first time the S_2LG phase line for this mixture. Since this phase line is terminated by the UCEP, with this data and the inflection point in the 58.5°C isotherm we can now locate the UCEP at 60.1°C and 235 bar. Our determination of the UCEP location is about 3°C lower than that reported previously by Paulaitis, et al. (46). However, the *in situ* nature of our NMR method allows us to precisely measure this UCEP temperature since we can determine the S_2LG phase line. These results indicate that our NMR technique can be greatly advantageous for solubility determinations near the UCEP. A more detailed analysis of our experimentally determined solubility data is now in progress.

Density and Temperature Effects on Collision Induced Scattering in Supercritical CO_2

In view of the importance of CO_2 in supercritical fluid extraction, we carried out an experimental study of the pressure and temperature effects on depolarized Rayleigh lineshapes in supercritical CO_2 (47). Collision induced scattering (CIS) is of considerable interest because it is a fairly unique probe of intermolecular interactions. Depolarized Rayleigh spectra (DRS) of dense atomic fluid and the DRS of spherical molecules have been extensively studied because the entire DRS of these fluids may be attributed to collision induced effects. For linear triatomics the interpretation of the DRS is necessarily more complicated as the time dependence of the polarizability anisotropy of the molecule will contain contributions from both the permanent anisotropy of the molecule, whose time dependence arises from molecular reorientation, and the induced polarizability which arises from multi-body interactions. The part arising from the permanent anisotropy may be referred to as the allowed part and the induced component as the non-allowed part. Despite these complications, significant progress has been made in the study of collision induced effects on the DRS of linear triatomics.

The results of our study were as follows. We obtained experimental data on the density dependence of the DRS of carbon dioxide at temperatures both above and below the critical temperature. By using Madden's theories (48-51) and the analogous results from other linear triatomics [CS_2 , COS] (17,18) as a guide, we showed the effects of CIS on the DRS of CO_2 . Lastly, we showed how failure to adequately account for CIS in the DRS of linear triatomics can cause ambiguity in the interpretation of the information on molecular reorientation present in the DRS.

Acknowledgments

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SUPERCRITICAL FLUID SOLVENT PROPERTIES AS A FUNCTION OF
TEMPERATURE AND DENSITY MEASURED BY THE SOLVATOCHROMIC METHOD

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INTRODUCTION

In the past few years supercritical fluids have attracted interest as solvents for both analytical and chemical process applications. They possess interesting combinations of solvent properties, such as high diffusivity and liquid-like solvating properties which can be drastically changed with moderate changes in temperature and pressure, making them attractive for a variety of uses.

One hindrance to the further development of supercritical fluid extraction or chromatographic techniques is that relatively little is known about the dependence of solvent properties of supercritical fluids, and fluid mixtures, upon various physical parameters. This study of the interactions between solutes and supercritical fluid solvents was aimed at extending the understanding of supercritical fluids as solvents, and to help in the selection of the most appropriate fluid for a particular application.

EXPERIMENTAL

Absorption spectra were measured on a Cary model 1605 spectrophotometer used in the dual beam mode. The measurements using liquid solvents were made using 1 cm square quartz cells with a solvent blank in the reference beam. The vapor and supercritical fluid spectra were taken versus air in the reference beam.

A specially constructed high pressure cell was used in taking the spectra in the supercritical fluid solvents. This cell has a cylindrical stainless steel body approximately 1" in diameter which has a 3/16" diameter hole drilled along the axis. Two connections for 1/16" tubing are present to allow for inlet and outlet flow. Each end of the cell has a seat for a 1/4" diameter 1/4" thick quartz window and is threaded to accept a brass nut. A 1/4" o.d. Teflon o-ring is placed on each side of each window to provide cushioning and a gas tight seal. The optical path between the windows was approximately 1/4". The absorption cell was wrapped with heating tape, insulated and equipped with a thermocouple. This arrangement allowed temperature regulation to within ± 0.5 C.

A Varian 8500 syringe pump was used to supply the supercritical fluid solvent at the appropriate pressure. The pump was connected to the cell via a Rheodyne valve equipped with a 10 μ l sample loop. A pressure transducer was connected to the cell outlet to allow accurate pressure measurement.

The experiments were conducted as follows: the sample was loaded in to sample loop and the valve switched to allow fluid from the pump to flow to the cell through the loop. A shut-off valve at the cell outlet was opened to allow solvent flow through the cell and the absorbance at a selected wavelength was measured to detect the appearance of the sample in the cell cavity. Often it was necessary to

partially purge the cell with additional solvent to decrease the sample concentration to the point that the absorbance measurement was on scale. When a usable concentration of sample had been obtained the outlet valve was closed and the absorption spectrum was taken under isobaric and isothermal conditions. After a scan the pressure or temperature was increased to the next level and the cell allowed to equilibrate at the new conditions before the next measurement. In all cases the spectrum of the pure fluid was also recorded to insure that there was no interference with the spectrum of the solute.

RESULTS AND DISCUSSION

Since interest centers on the specific interactions between solute and solvent, and how those interactions change as the density and composition of the supercritical fluid solvent are varied, an experimental technique is needed which is sensitive to the cybotactic environment of the solute. One such technique is the solvatochromic method, which probes the effect of solvent on the optical absorption spectrum of the solute molecule (1).

Using the solvatochromic method to study solvent effects of supercritical fluids is particularly efficacious in view of the extensive work of Taft and coworkers in measuring the solvatochromic shifts of a large number of solute molecules in a wide range of liquid solvents (2). They have been successful in developing a π^* solubility scale which encompasses a wide range of solute types and which can account for variance in several solvent properties, including polarity, polarizability, hydrogen bonding ability, etc.

The π^* polarizability scale was originally developed from observations of solvent effects on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the probe molecules. By using a select group of solutes and solvents which minimized hydrogen-bonding, Taft and co-workers were able to relate solvent polarity to relative shifts in the position of the absorption maximum. These data were primarily dependent on the interaction between solute and solvent dipoles. Further refinements have since been made to account for solvent-solvent interaction, the presence of induced dipoles, and hydrogen bonding between solute and solvent (3).

Since the π^* scale is well established for the study of conventional solvents it may afford a convenient basis for the comparison of liquid and supercritical solvents. Further, by determining the various scale parameters for these fluids it should be possible to obtain some insight into the specific solvation mechanisms involved, and how those mechanisms change as the solvent composition and conditions are altered.

The compounds 2-nitroanisole (2NA) and 4-ethylnitrobenzene (4ENB) were chosen to be the initial probe molecules in our initial solvatochromic studies of supercritical fluid solvents. These compounds have been previously used by Taft et al. in the studies of conventional liquid solvents, thus making it easier to integrate supercritical fluid solvents into the π^* solvent polarity scale. It is also advantageous that these compounds are liquids and have absorption maxima at convenient wavelengths in the UV.

The maxima of the absorption spectrum of each of these compounds are shifted in wavelength when in liquid solvents of varying polarities (Table 1). The position of the absorption band of the vapor (essentially a solvent with no polarity or hydrogen bonding ability) is used as a reference. As the solvent becomes more polar the absorption maximum is shifted to longer wavelengths (lower energies). This type of shift indicates that the excited electronic state is being stabilized

TABLE 1. Wavelength of Absorption Maximum of 2NA and 4ENB in Various Solvents

Solvent(a)	2NA		4ENB	
	Observed(b)	π^* (c)	Observed	π^*
Vapor	286	285	250	251
CO ₂ (a)	295	--	257	--
N ₂ O(a)	297	--	--	--
CClF ₃ (a)	299	--	--	--
NH ₃ (a)	303	--	260	--
Pentane(d)	306	305	263	265
Tetrahydrofuran	318	312	273	275
Acetonitrile	324	325	276	278
Methanol	322	322	272	275

(a) The supercritical fluids (CO₂, N₂O, CClF₃, and NH₃ had $T_r = 1.01$ and $P_r = 1.05$.

(b) Observed wavelength of absorption maxima, in nm.

(c) Predicted by π^* scale using parameters from Table 2.

(d) Predicted wavelength using parameters for heptane.

with respect to the ground electronic state, thus decreasing their energy gap. These results are in accord with the prediction of the π^* model when the proper coefficients are used for each of the solutes and solvents (Table 2) (4).

Having established the behavior of the probe molecules in conventional solvents, it is possible to compare their behavior in some common supercritical fluids. It is evident from Table 1 that supercritical fluid solvents at moderate reduced temperatures and pressures have relative solvating abilities in accordance with their polarities. The less polar fluids CO₂, N₂O, and CClF₃ (Freon-13) shift the absorption maxima to an intermediate position between that measured in the vapor phase and pentane. NH₃ is more polar and the wavelength of the maximum falls close to that of pentane.

The interest in using supercritical fluids as solvents for extraction processes and chromatography is in great extent due to the fact that it is possible to change the solvent properties of the fluid by changing the density and temperature. A large part of the interest in using the solvatochromic method to study these solvents is to see if it is possible to observe and quantify these changes in solvating ability via the absorption shift.

TABLE 2. π^* Solubility Scale Parameters

Solvent	π^*	Solute	ν_0 (cm ⁻¹)	-s
Vapor (4)	-1.06	2NA (2)	32.56 kK	2.428
Heptane (4)	-0.08	4ENB (2)	37.60 kK	2.133
Tetrahydrofuran(4)	0.58			
Acetonitrile(4)	0.75			
Methanol (3)	0.60			

Figure 1 shows that the wavelength of the absorption maximum changes most rapidly at pressures just above the critical pressure. This observation can be explained by examining the relationship between pressure and density is a non-linear function of pressure, and changes most rapidly at reduced pressures near 1. The data are re-plotted in Figure 3 to illustrate the relationship between the energy of the transition (in wave numbers) and the fluid density. This plot also contains data obtained by maintaining a constant pressure and varying the temperature to change the density. It is apparent from this data that fluid density, and not temperature, is of primary importance in determining the amount of spectral shift. This correlation with fluid density is in agreement with the predictions of numerous solubility studies. Finally, Figure 4 shows how the absorption maximum varies with pressure for 2NA in NH_3 .

Clearly, the solvatochromic method holds promise for comparison of supercritical fluid solvents with conventional liquid solvents, due to sensitivity to changes in solvation arising from varying the density of the fluid solvent. By using the data on pure fluid solvents as a foundation it should be possible to extend this work to the study of mixed supercritical fluid solvent systems. Since this technique probes the cybotactic environment of the solute it should be feasible to determine how the solvating power of a fluid changes as small amounts of a modifier are added.

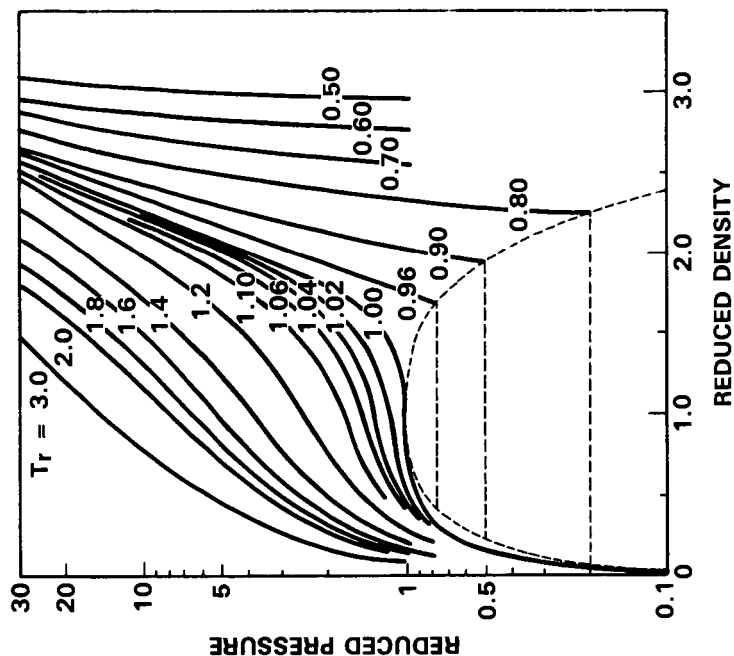
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TYPICAL PRESSURE-DENSITY BEHAVIOR



T_r = REDUCED TEMPERATURE

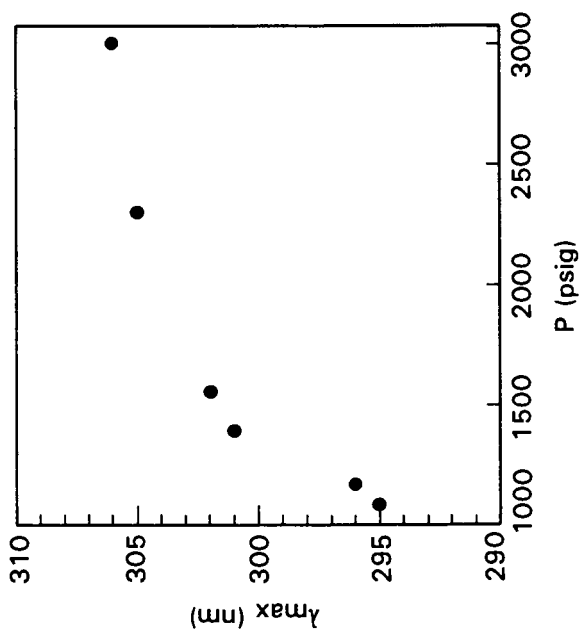


FIGURE 1. 2-Nitroanisole in CO_2 . Temperature = $50^\circ C$.

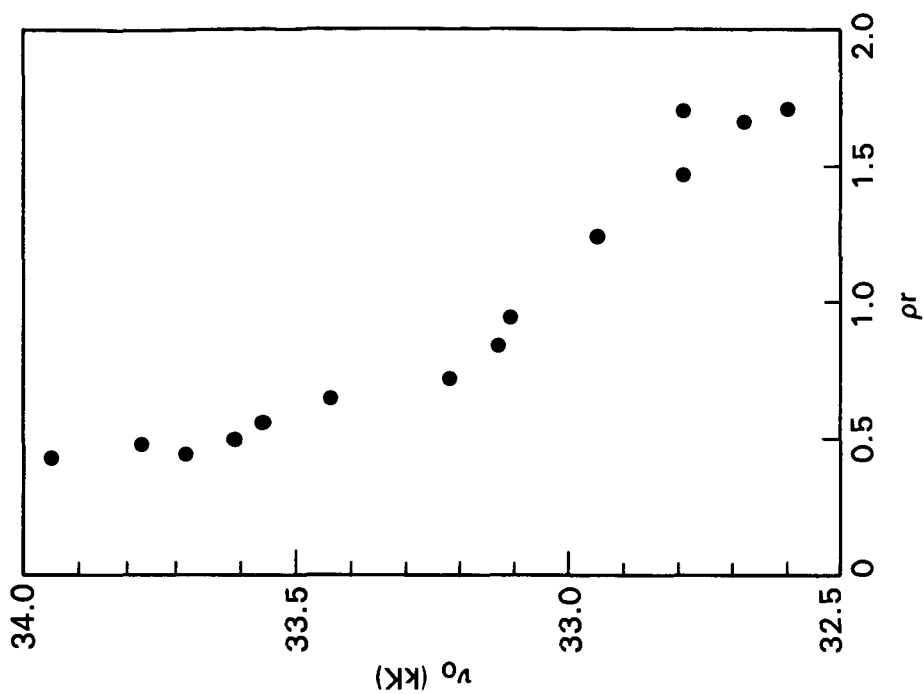


FIGURE 3. 2-Nitroanisole in CO_2 .

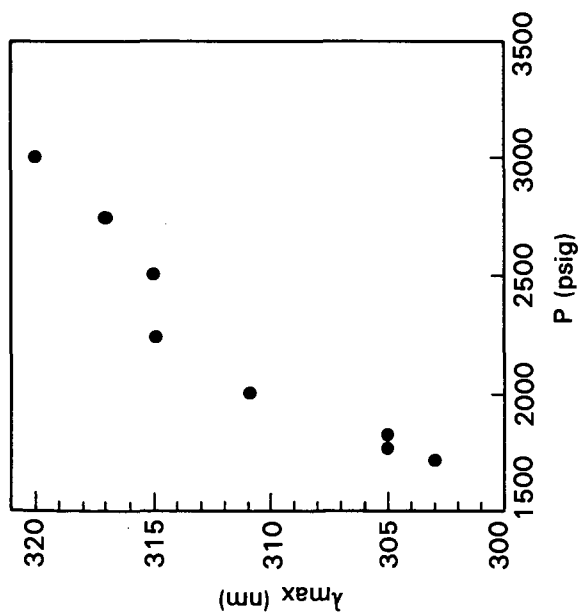


FIGURE 4. 2-Nitroanisole in NH_3 . Temperature = 140°C .

Mixed Supercritical Solvents for Selective Solubility Enhancement

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Supercritical fluids have generated a great deal of interest in the chemical engineering community for a variety of applications, including enhanced oil recovery, resid upgrading, and extraction (1). This being the case, we have been involved in an intensive program designed to understand both qualitatively and quantitatively the complex phase behavior inherent in mixtures of solutes dissolved in supercritical solvents.

This program involves measurements on thermodynamic modeling of selected supercritical systems. Our work first involved analysis of solutes dissolved in pure supercritical fluids to determine what differences, if any, solute nature had on the solubility behavior. Our data analysis requires two properties of the solute: first, its solubility in the selected supercritical fluid, second, the solute sublimation pressure at system temperature. Combining these two quantities yields the enhancement factor

$$K = \frac{y_2 P}{P_{2 \text{ sat}}} \quad 1)$$

which is simply a dimensionless solubility that scales out the saturation pressure contribution to the solubility. Comparison of enhancement factors (not solubilities!) yields the true solution behavior of the various solutes used in these studies.

We have compared enhancement factors for a variety of solid compounds of different polarities and functionalities in pure supercritical fluids and have found that the solution behavior is relatively insensitive to the chemical nature of the solute species. Thus, as Figure 1 illustrates, the solution behavior of the solutes phenanthrene and acridine is virtually identical, even though acridine has a relatively large dipole moment at 2.1 Debyes and is a heterocyclic analogue to the base pyridine. To understand why this is so, a rough order of magnitude calculation was performed to determine the relative magnitudes of the various forces involved in this system. Table 1 shows that the contribution from polar forces, e.g. those dipole/induced dipole forces between the acridine and CO_2 molecules, is only one one hundredth that of the contribution from non-specific van der Waals forces, which should be nearly identical for the acridine/ CO_2 and phenanthrene/ CO_2 systems. Since the forces involved in solutions of pure fluids arise almost exclusively from these van der Waals forces, one expects the solubility behavior to be the same in the class of solutes we have studied.

It is apparent that to induce some differentiability into the solution behavior, one will need to either use some associating fluid (such as ammonia) or modify the supercritical fluid by adding chemical "entrainers" to the solution. We have begun such studies in which dilute (1-5%) concentrations of polar entrainers are added to the bulk supercritical phase (CO_2). Dilute solutions are necessary for two reasons. First and foremost is the fact that dilute solutions allow us to operate over a broad range of pressures and temperatures without having to be concerned with separation into entrainer-rich and CO_2 -rich phases; we can be assured that we always have a single, homogeneous phase. The second reason concerns the fact that while we would like to modify the fluid's solution behavior, we also wish to leave its useful phase behavior as intact as possible.

The two entrainers chosen were methanol and acetone. Both are small, relatively polar molecules which go into solution with CO₂ readily (2,3). Methanol, with its hydroxyl proton, is also a likely candidate for hydrogen bond formation with proton accepting species.

The entrainer effect can be quite large, as seen in Figure 2, where we show the solubility increase of the solute acridine in doped SCF's. This figure shows an over 500% increase in the solute's solubility over that in a pure supercritical solvent. Of even greater interest is the fact that this solubility increase is quite sensitive to the chemical nature of the solute species involved; Figure 3 illustrates this behavior. Here, the highly polar species acridine and fluorenone are seen to have solubilities greatly promoted by the presence of the entrainer methanol in supercritical CO₂. The much less polar species dibenzofuran is promoted to a much lesser extent, and the non-polar species phenanthrene and fluorene show virtually no solubility promotion in the entrained solvent. This behavior is in marked contrast to that of pure SCF's, where there is little if any solvent selectivity to these solute species.

As Table 1 illustrates, the relative magnitudes of the dipole-dipole and dipole-forces between a polar solute and polar entrainer molecule do not appear to be great enough to account for this solubility increase if the entrainer were randomly dispersed within the fluid. This suggests an aggregation or clustering of the entrainer species around the solute molecule in solution. Spectroscopic information is needed, however, to confirm this speculation.

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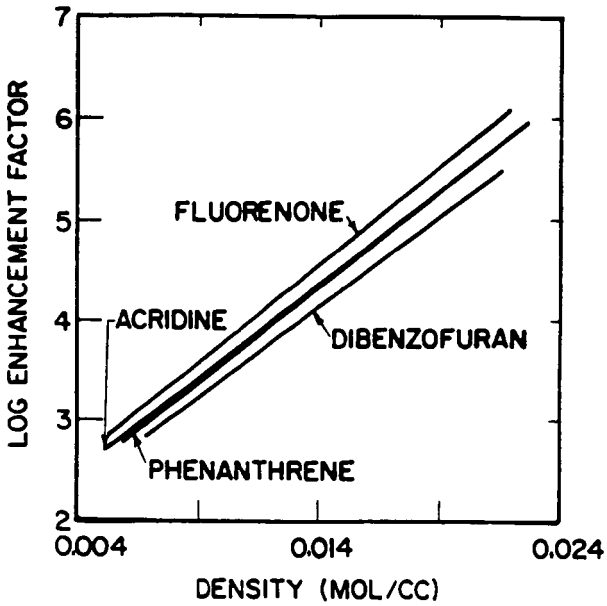
- (1) Paulaitis, M. P.; Krukonis, V.; Reid, R.; Kurnik, R.; Reviews in Chemical Engineering, 1 (2), 1983, 179.
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- (4) Prausnitz, J. M.; "Molecular Thermodynamics of Fluid Phase Equilibria", copyright 1969 Prentice-Hall, Englewood Cliffs, NJ.

TABLE 1

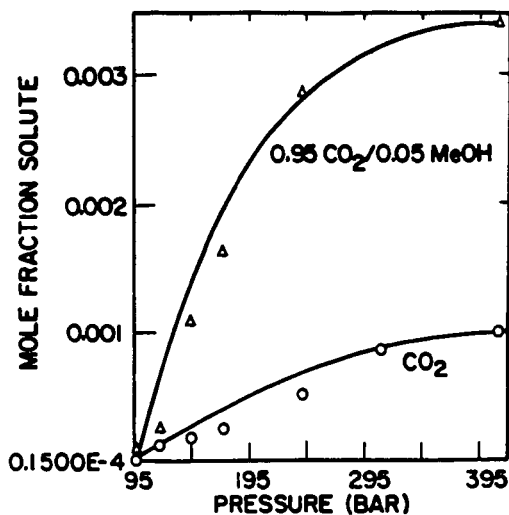
RELATIVE MAGNITUDES OF INTERMOLECULAR FORCES (4)

System: acridine/CO₂/acetone

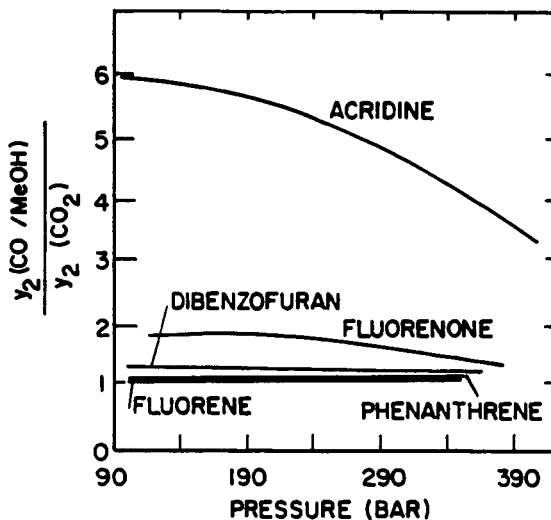
CO ₂ disp	CO ₂ ind dip	acetone disp	acetone ind dip	acetone dip/dip
1	.01	.89	.30	.27



ENHANCEMENT FACTOR FOR SEVERAL
SOLUTES IN CO₂ AT 323 K



**INCREASE IN SOLUBILITY WITH ENTRAINER-DOPED
SOLVENT SYSTEM : ACRIDINE @ 323 K**



**ENTRAINER EFFECT WITH VARIOUS SOLUTES
5 mole % MeOH/CO₂ @ 323 K**

ELECTROCHEMISTRY IN SUBCRITICAL AND SUPERCRITICAL WATER
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Introduction

Supercritical fluids have received significant interest recently because of their unique solvent properties. Gases such as carbon dioxide and ethylene have been used to perform a number of difficult separations. Some of these processes, for example the decaffeination of coffee, have been commercialized (1).

Water has not been studied extensively for use as a supercritical solvent because of the high temperature and pressure of its critical point ($T_c = 374^\circ\text{C}$, $P_c = 221$ bar). We are performing electrochemical research in supercritical water to take advantage of its unusual properties. The areas of study include the effect of temperature on the electrochemical potential of ions in water and the electrochemical reaction of organic compounds in aqueous solution.

The chemical behavior of an ion in water is of course influenced by water molecules that are oriented around it. A change in the structure of the solvation sphere around an ion will affect the electrochemical potential of the ion. Such a change in structure can be achieved by heating water to the critical region where the internal structure of hydrogen bonding is very sensitive to temperature changes. In this region, the electrochemical potential can also be a strong function of temperature. A study of these potential shifts should provide insight into the structure of solvation spheres in water and of water itself.

At high temperature, the breakdown of hydrogen bonding in water greatly reduces the dielectric constant. At the critical point, the dielectric constant of water is 3, approximately the same as that of benzene. Not surprisingly, water becomes miscible with non-polar organics at high temperatures. In the miscible region, it is possible to react organics electrochemically without using the more toxic and expensive organic solvents that are necessary for dissolution at 25°C . While many compounds will decompose in high temperature water, others, which are not active at normal conditions, will become subject to electrochemical attack at high temperature.

Though no definite predictions can be made, supercritical water appears to be a promising area for study. A cell has been designed which will operate at supercritical conditions, and preliminary data have been obtained for electrolyte solutions.

Experimental

The high temperature section of the electrochemical cell is made of an aluminum oxide ceramic. The volume of heated solution is less than 1 cm^3 , so the stored energy of the system is very small. All measurements were made with the solution stationary in the cell, but a high pressure pump allows the cell to be flushed with fresh solution. This prevents reaction products from contaminating the electrolyte. The platinum working and silver reference electrodes are in close proximity in the heated zone. The working electrode area is approximately $3 \times 10^{-4}\text{ cm}^2$. The platinum counter electrode is in a cool region downstream from the heated zone. All seals are made of teflon, and are in unheated parts of the cell.

Results

Cyclic voltammetry has been carried out in solutions of $0.05\text{M H}_3\text{PO}_4$, 0.2M NaHSO_4 , and 0.2M KCl . The pressure was held at 240 bar while the temperature was varied. The scan rate was 200 mV/sec .

In $0.05\text{M H}_3\text{PO}_4$, the potential difference between the evolution of hydrogen and

oxygen declined from 1.7 V at 25°C to 1.0 V at 375°C. At high temperature, the solution resistance increased dramatically indicating the dissociation of the acid was declining.

In 0.2M NaHSO₄, the potential difference between the evolution of hydrogen and oxygen declined from 2.0 V at 25°C to 1.3 V at 375°C.

In 0.2M KCl, the potential difference between the evolution of hydrogen and oxygen declined from 1.8 V at 25°C to 1.6 V at 300°C. The potential difference between the chloride/chlorine couple and oxygen declined from 0.2 V to <0.1V over this same temperature range.

Summary

The data presented here represent the first steps into a new area of electrochemistry. Much more data will be necessary before any major conclusions can be drawn. Even so, these results do show that electrochemistry can be carried out under near critical and supercritical conditions, and that there are significant changes in the behavior of ions in solution.

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ORGANIC CHEMISTRY IN SUPERCRITICAL FLUID SOLVENTS:
PHOTOISOMERIZATION OF trans-STILBENE

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INTRODUCTION

The unusual solvent properties of supercritical fluids (SCF's) have been known for over a century (1). Just above the critical temperature, forces of molecular attraction are balanced by kinetic energy; and fluid properties, including solvent power, exhibit a substantial pressure dependence. Many complex organic materials are soluble at moderate pressures (80 to 100 atmospheres); and SCF solvent power increases dramatically when the pressure is increased to 300 atmospheres. The pressure responsive range of solvent properties thus attainable has provided the basis for investigating the fundamental nature of molecular interactions and, more recently, for exploitation of supercritical fluids in areas of applied research (2,3).

In the latter activity, supercritical fluids have been utilized extensively in the thermochemical solubilization of coal (4), for selective extraction of naturally occurring materials (5,6), and in various separation techniques including distraction (7) and supercritical fluid chromatography (8,9). The physicochemical principles underlying these applications have also been investigated (10). In view of the high level interest in manipulating complex organic mixtures with supercritical fluids, it is surprising that these fluids have seen little use as solvents for organic reactions (11,12). The pivotal role of solvent properties in controlling the course and rate of chemical reactions is well established (13); and, thus, the same kind of pressure responsive solvent-solute interactions which control extractions and separations in SCF's can be expected to direct chemical pathways and influence reaction rates.

Moreover, much of our understanding of the nature of chemical reactions has been derived by observing the responses of these processes to changes in solvent properties. While investigations of this type have been highly productive, interpretation of the results has often been blurred by uncertainties inherent in the experimental approach. Heretofore, liquid solvents have been used in these investigations, and solvent properties have been changed by adjusting the solvent composition. Unfortunately, no quantitative relationship between bulk solvent properties and chemical phenomena has emerged, presumably due to selective solvent-solute interactions which result in differences between bulk solvent composition and microscopic solvent composition (13).

In contrast to liquid solvents, the properties of a single SCF solvent can be altered over a wide range through modest manipulations of pressure and/or temperature. Thus, SCF's provide an opportunity to investigate the effects of solvent properties on chemical reactions without changing the solvent composition. Experimentally, in order to

induce the greatest response of solvent properties to changes in pressure, it is generally best to operate at a constant reduced temperature, T_R , between 1.0 and 1.1 and to vary the reduced pressure, P_R , between 1.0 and 3.0 (14).

For several reasons, we chose carbon dioxide for these initial investigations. In the first place, the properties of supercritical carbon dioxide are well known, and the solubility of a relatively large number of organic materials have been examined in this medium. Secondly, although carbon dioxide is interactive with solute molecules, it is generally unreactive. Finally, the supercritical working range ($1.0 < T_R < 1.1$), 31.5 to 60°C, is experimentally convenient; and many organic reactions have been extensively investigated in this temperature range.

Investigations of organic reactions in supercritical solvents are subject to several constraints, one attributable to supercritical fluid properties and others imposed for interpretive and experimental simplicity. Because supercritical fluid properties are affected by changes in temperature, a reaction should be selected which does not require heat for initiation and is not highly exothermic. Secondly, for experimental simplicity and clarity of interpretation, a clean, well understood reaction should be chosen; and one should expect an experimentally observable response to changes in pressure. Finally, a unimolecular reaction which produces a single product obviates the complication of controlling the concentrations of two reactants and simplifies product analysis. The photoisomerization of trans-stilbene meets these requirements.

The photoisomerization of stilbene is one of the most extensively studied and best understood photoreactions (15). Solvent effects have been thoroughly investigated for both the direct and photosensitized isomerizations, and a model has been developed which attributes these effects to solvent viscosity (16). Increased viscosity inhibits direct photoisomerization of the cis isomer, but facilitates that of trans-stilbene. As a result, the cis/trans ratio of the photostationary state increases with increasing solvent viscosity. The wide range of viscosities which are attainable by pressure manipulation of supercritical carbon dioxide provides an excellent opportunity to probe the effect of viscosity on stilbene photochemistry in the same solvent.

EXPERIMENTAL

Construction of the SCF photochemical reactor and experimental techniques are described elsewhere (12). Photoisomerizations were carried out using a 450 watt Hanovia medium pressure mercury source, and each reaction was followed to the photostationary state by gas chromatographic determination of the cis/trans ratios.

RESULTS & DISCUSSION

A widely used method for assessing supercritical fluid phenomena consists of comparing physical and chemical behavior above the critical point with corresponding behavior in the subcritical liquid. Because this approach (unrealistically) seeks to observe discontinuous behavior between states, the results of such experiments are often ambiguous. In the present study, we have compared the photoisomerization of trans-stilbene in subcritical and supercritical CO₂; and, as a

model for condensed phase behavior, we have also carried out these isomerizations in cyclohexane. In all three systems, we have probed and compared the effects of temperature, concentration, and, most significantly, pressure on the photostationary state as reflected in the cis/trans ratio. The results from these experiments are shown in Tables 1 and 2 and are plotted in Figures 1 through 3.

From the results obtained in cyclohexane (Table 1), it is clear that, in the condensed phase, we can expect very little effect on the photostationary state due to changes in temperature or concentration. On the other hand, these factors cause large changes when the reaction is carried out in liquid or (especially) SCF CO₂. The contrast in behavior is even more apparent in Figures 1 and 2.

Table 1. Photoisomerization of trans-Stilbene in Cyclohexane^a

Initial Concentration (mg/ml) ^b	Temperature (°C)	Irradiation Time (Minutes)	Photostationary State (cis/trans)
2.14	21.7	70.0	6.1
2.14	40.0	70.0	6.1
1.07	21.7	20.0	6.9
1.07	40.0	30.0	6.9
0.50	21.7	10.0	6.4
0.50	40.0	15.0	6.7
0.25	21.7	10.0	6.4
0.25	40.0	5.0	6.6

a. Direct irradiation with a Hanovia 450 watt medium pressure mercury vapor lamp.

b. Pure trans-stilbene was used.

Table 2. Photoisomerization of trans-Stilbene in Carbon Dioxide^a

Initial Concentration (mg/NL) ^b	Reactor Concentration (mg/ml) ^c	Temperature (°C)	Photostationary State (cis/trans)
2.00	0.98	25	8.63
2.00	0.87	40	8.68
0.80	0.39	25	7.15
0.40	0.20	25	6.42
0.40	0.17	40	6.73
0.28	0.13	35	5.66
0.28	0.12	40	6.54
0.28	0.11	50	7.04
0.24	0.10	40	6.29
0.12	0.052	40	4.80

a. Irradiation in a flow reactor with a 450 watt Hanovia medium pressure mercury vapor lamp.

b. Pure trans-stilbene was used. Normal liter (NL): the quantity of CO₂ which has a volume of 1 liter at 25°C and 1 atmosphere.

c. Calculated from the reported density of pure CO₂.

In Figure 3 is shown the effect of pressure on the cis/trans ratio. While there is a noticeable effect on liquid CO₂, the dramatic response of the ratio to decreases in pressure gives us a clear signal that we can expect to manipulate chemical pathways, rates, and equilibria in the SCF state. This will be the focus of future studies.

ACKNOWLEDGEMENT

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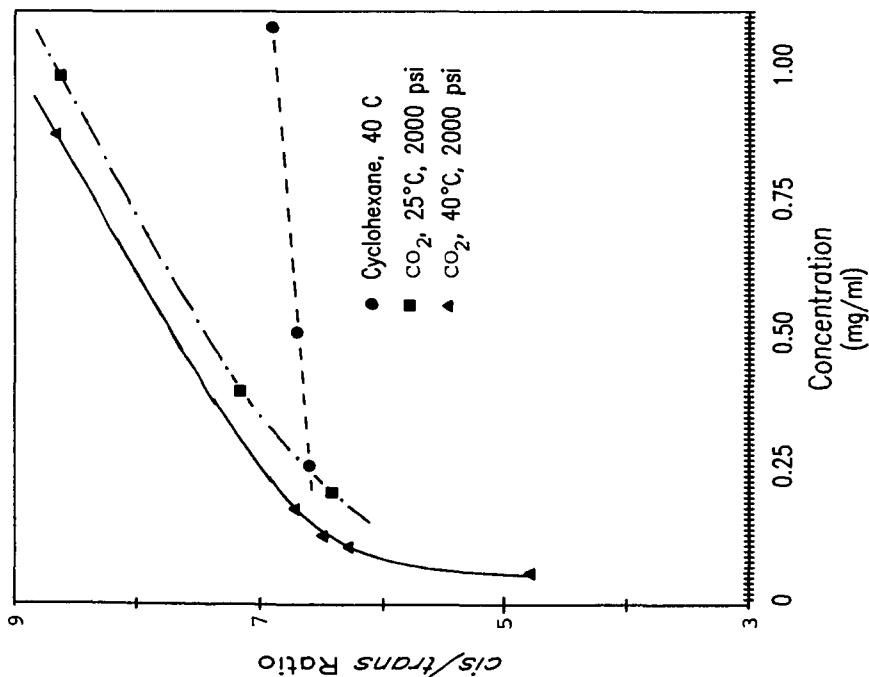


Figure 1. Concentration Effects in the Photoisomerization of *trans*-Stilbene.

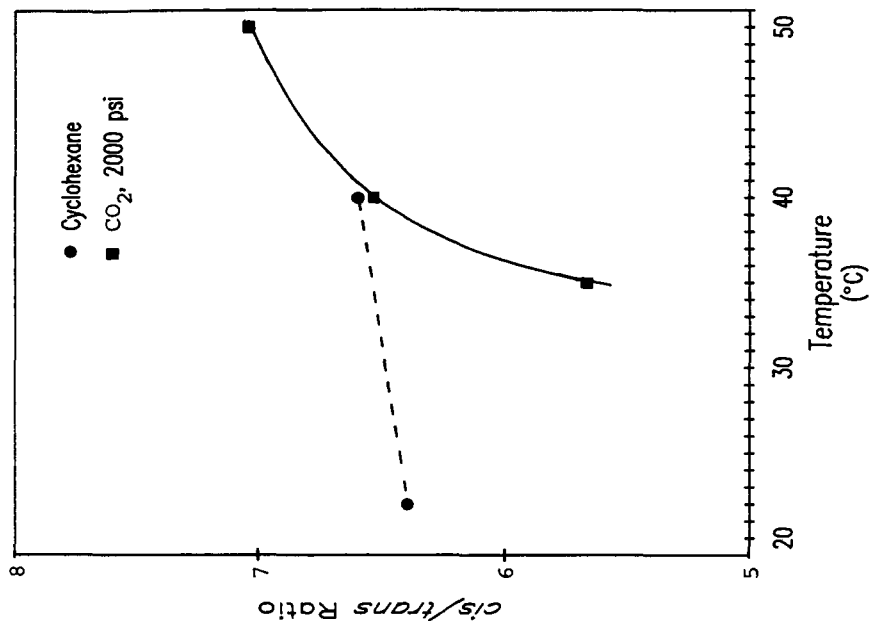


Figure 2. Temperature Effects in the Photoisomerization of *trans*-Stilbene.

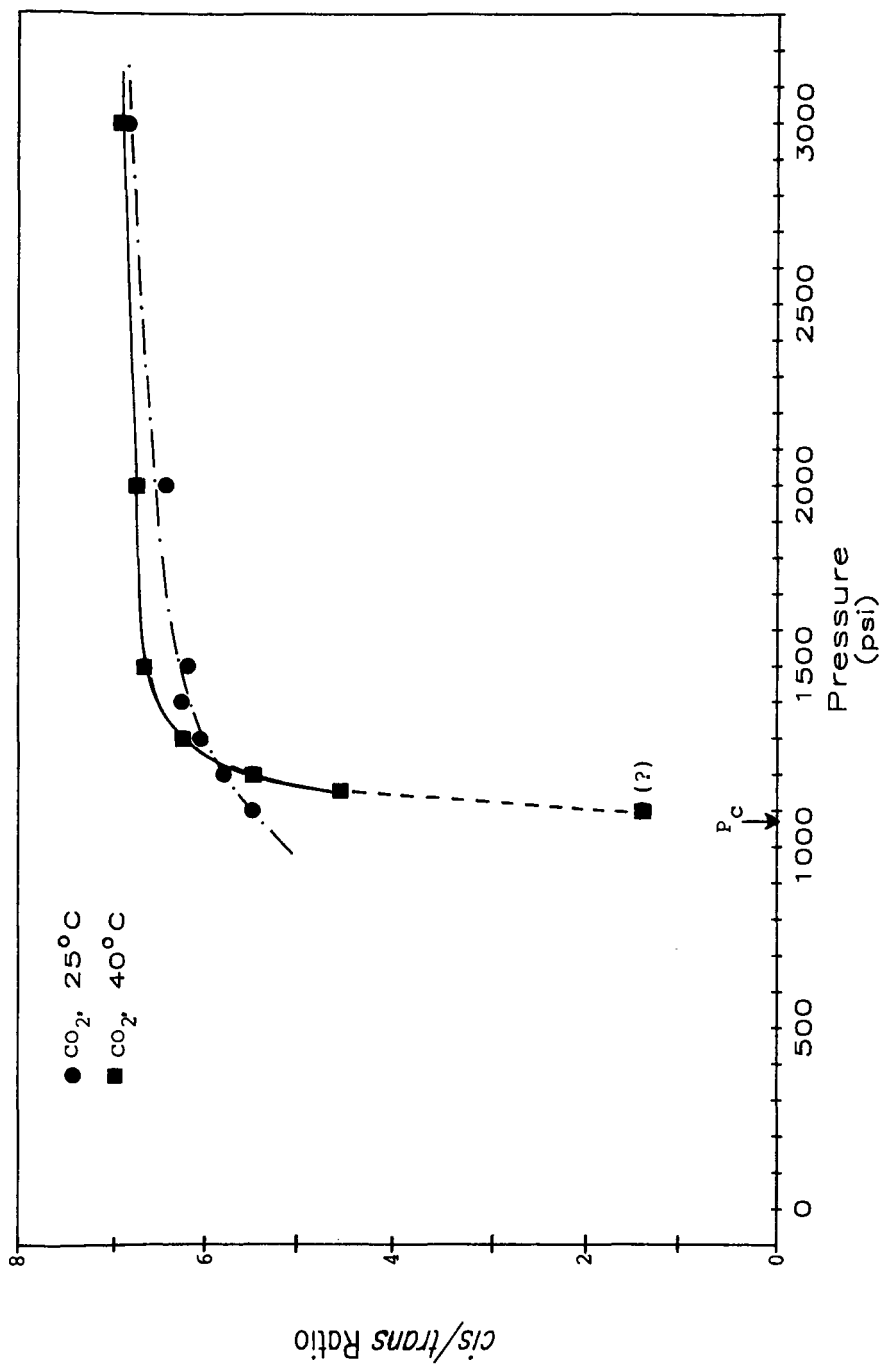


Figure 3. Pressure Effects in the Photoisomerization of trans-Stilbene.

EFFECTS OF SUPERCRITICAL SOLVENTS ON THE RATES OF HOMOGENEOUS CHEMICAL REACTIONS

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Discussion

A number of recent reviews describe supercritical fluid extraction (1,2,3), however, the literature contains relatively few examples where supercritical fluid solvents have been used to modify or control reaction rate constants. Liquid phase reactions have been studied over wide pressure ranges, e.g. 1-10 kbar, to determine activation volumes, i.e. the pressure derivative of the rate constant. These studies essentially ignore the highly compressible near supercritical region where activation volumes can become infinite, either positively or negatively.

It is ironic that the large growth in SF extraction at the Max Planck Institute in Germany in the 1960's was the result of a serendipitous discovery of the solvent power of supercritical ethylene during the "Aufbau" reaction of triethylaluminum with ethylene (4). The literature contains few examples where supercritical fluids have been used as a medium to modify or control reaction rate constants (5,6,7).

Simmons and Mason (7) observed an abrupt decrease in Δv^\ddagger near the critical conditions for the cyclic dimerization of C_2F_3Cl . It is due to the large negative partial molar volume of the dimer in the transition state. At 120°C, the rate constant doubled for a pressure increase from 43 to 53 bar. Paulaitis (6) measured activation volumes as low as -500 cc/mol for the Diels-Alder cycloaddition of isoprene and maleic anhydride in CO_2 . The rate constant increased about 60% for a change in pressure of several bar. The pronounced solvent effect is due to the large dipole moment of the transition state, which is on the order of 3-7 Debye for other dienes with maleic anhydride (8).

The objective is to measure and to predict the effects of supercritical fluid solvents on reaction rate constants. In the near critical region, all of the density dependent variables such as the dielectric constant, refractive index, fugacity coefficient, and solubility parameter are extremely strong functions of temperature and pressure. This sensitivity, which is used advantageously in supercritical fluid extraction, could also be exploited in reaction processes. For example, rate constants could be changed orders of magnitude using modest changes in the temperature and pressure in the critical region. A UV-visible spectroscopic technique has been applied to supercritical fluids for the first time to determine the solvent polarity as a function of temperature and pressure. Solvent polarity scales based on solvatochromism, i.e., shifts in the absorption wavelength of indicator dyes caused by the solvent, are used commonly to correlate and to predict rate constants for liquid phase reactions. Novel processes could be developed using supercritical fluid solvents to achieve and control the desired selectivity in parallel reactions, the yield in reversible reactions, and to recover and purify reaction products efficiently using supercritical fluid extraction.

Conclusions

For dyes such as phenol blue, solvatochromic shift data provide a sensitive indication of the structure and polarity of supercritical fluid solvents. The polarities of supercritical ethylene and liquid hexane become equivalent for a density ratio of C_2/C_6 of 2.7 since the latter is more polarizable. At 25°C and 66 bar, the data were used to predict that the activation volume is -5000 cc/mol for the Menshutkin reaction of tripropylamine and methyl iodide. This large negative value is due to the high compressibility of SF ethylene in the critical region. These results suggest that rate constants may be altered markedly in SF solvents using small changes in

temperature and pressure.

The theory of solvent effects on electronic spectra can be extended to the SF state by including the effects of the isothermal compressibility. The local density of the SF solvent about the solute can be obtained by comparing the experimental E_T with the intrinsic value, E_T^0 , which is calculated straightforwardly for incompressible liquids. At the bulk density, the polarity of the SF solvent is equivalent to that of a hypothetical reference liquid at the local density. The specific polarity, which is due to hydrogen bonding, may be obtained by comparing this hypothetical reference fluid with the experimental data. For CF_3H , the specific polarity appears to be less sensitive to density than the intrinsic polarity. The understanding of the polarity of SF solvents at the microscopic level will benefit the development of both extraction and reaction process at SF conditions.

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Flow Adsorption Calorimetry with Supercritical Fluids on Silica Gel

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The supercritical state has long held a fascination for chemists as a "fourth state of matter."^{1,2} Recently, it has been recognized that supercritical extractants are also of industrial value and play an important role in geochemical and extraterrestrial chemistry.^{3,4} Of particular significance is the use of supercritical carbon dioxide for tertiary oil recovery, coal extraction, and chromatography in all of which supercritical fluids interact with solid phases.⁵⁻⁸ In the course of a thermometric study of solid acids with basic solutions we became interested in determining heats of adsorption by flow calorimetry and extending this to elevated temperatures and pressures.

The apparatus shown in Figure 1 may be assembled, for the most part, from readily available components following recent accounts of high pressure, and high temperature flow calorimeters assembled for heats of mixing.⁹⁻¹¹

After preliminary calibration of the calorimeter under various batch conditions by heats of solution of KCl and BaCl₂ in water¹² and heats of immersion of silica gel in water¹³, and ΔH_{ads} of isopropylamine from an isopentane solution was determined on silica gel using again heats of immersion (batch mode) at ambient temperature (Table I) to establish standards of reference for the more difficult flow studies.

TABLE I

ΔH_{imm} (Batch Mode) of Silica Gel in Some Liquids at 26°C

Liquid	$\Delta H_{imm}/\text{cal g}^{-1}$	$T_c/^\circ\text{C}^a$	P_c/psi^a
(1) Isopentane	-4.83 ± 0.63	187.8	483.5
(2) 10% Isopropylamine	-21.66 ± 0.81	190.0 ^b	527.0 ^b
(3) Isopropylamine	-20.33 ± 0.30	209.7	700.0 ^c

$$(2) - (1) = \Delta H_{ads} = -16.83 \pm 1.02 \text{ cal g}^{-1}$$

$$\Delta H_{ads} \text{ (flow mode) at 30 PSI} = -17.97 \pm 0.27 \text{ cal g}^{-1}$$

a. Ref. 16

b. Ref. 17

c. Ref. 18

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Table II presents ΔH_{ads} values of isopropylamine on the same sample of silica gel (Fisher grade 62) from an isopentane carrier stream over a range of temperatures and pressures from subcritical to supercritical. Results are given in terms of calories per gram of silica gel. Since this is a saturation experiment, the observed values at a given temperature and pressure should be (and are) independent of flow rate (7-30 ml/hr) or concentration (10-20%) of isopropylamine.

TABLE II

Heats of Adsorption, ΔH_{ads} of Isopropylamine on Silica Gel at Different Temperatures and Pressures by Flow Calorimetry

Temp. (°C)	P (PSI)	ΔH_{ads} (cal/g)
26	30	-17.97 ± 0.27
	1000	-17.44 ± 0.84
80	500	-15.79 ± 0.22
	1000	-15.34 ± 0.23
160	500	-12.52 ± 0.80
200	500	-9.86 ± 1.30
	1000	-11.52 ± 0.72
	1500	-13.61 ± 0.16
250	1000	-4.30 ± 0.16

The most obvious results from Table II are: a) The insignificant effect of pressure on ΔH_{ads} in the subcritical range. b) The decrease of ΔH_{ads} in response to increasing temperature at a given pressure. c) The significant increase in ΔH_{ads} with increase in pressure above the supercritical threshold at 200°C. These observations are consistent with the notion that isopropylamine, a strong base, is primarily chemisorbed on the silica gel surface by hydrogen-bonds.¹⁴ Increasing the temperature weakens this interaction. However, close to the critical temperature, a small increase in pressure results in a substantial increase in density causing an increase in the effective concentration of the base. Thus, an increase in pressure above the critical temperature manifests itself as an increase in the ΔH_{ads} . It remains to be seen how less strongly adsorbed materials will respond to crossing into the supercritical region.

A crucial component for extending flow calorimetry into the supercritical range is the use of a Setaram-80 heat flow calorimeter which may be operated in the flow mode at temperatures up to 300°C using the sample cell (5) in Figure 1. This was designed for adsorption thermochemistry so that a bed of adsorbent in cell (5) can be placed downstream from the switching valves in the pumps so that either of the fluid streams leaving the piston pumps (A and B) may be directed through the adsorbent bed. An important problem in flow calorimetry (even at ambient conditions) is to balance mass transfer and heat transfer.¹⁵ Unless the stream of fluid containing the adsorbate has been

brought to exactly the temperature of the adsorbent (in cell 5) the observed ΔH_{ads} will contain a contribution due to incomplete thermal equilibration of the streams. Figure 2 shows how this problem was solved by forcing the stream through a coil of 1/8" (OD) x 0.60" (ID) 316 stainless steel tubing positioned in the preheating chamber of the calorimeter.

In each experiment, about 100-150 mg. of silica gel was used. After initial cleaning with methanol followed by hexane, the system was then purged with N_2 for about 10-15 min. before the assembled cell was put in line. The system was brought to the appropriate pressure by pumping an inert solvent (isopentane) at 75 ml/hr and adjusting the back pressure regulators. Once the appropriate pressure was obtained, the solvent flow rate was reduced to either 7 or 15 ml/hr and then the system was thermally equilibrated as demonstrated by a steady baseline on the recorder. Once a steady baseline was achieved, the reactive liquid in pump B was pressurized while still closed to the system to avoid a pressure drop and backflow when switching pumps. Simultaneously, pump A was turned off and pump B was opened to the system at the same flow rate as that of pump A. Heat evolved during the process of interaction of the isopropylamine with the silica gel was monitored by both digital and analog outputs, and was presented as an exothermic release of heat up to the point of surface saturation after which the system returned to its original baseline temperature in about 30 min.

ACKNOWLEDGEMENTS

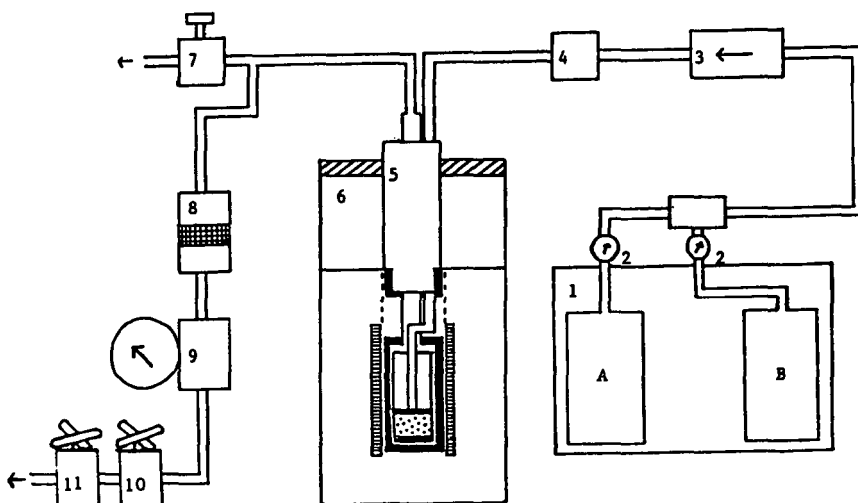
This work was made possible through grants from the Exxon Educational Foundation and the Department of Energy (Contract No. FG22-82PC50807) to E.M.A. and the National Science Foundation (Grant CHE-8119600 to C.H.L.). We are glad to acknowledge the expertise of Mr. Milton L. Whitfield in the Duke Physics Shop.

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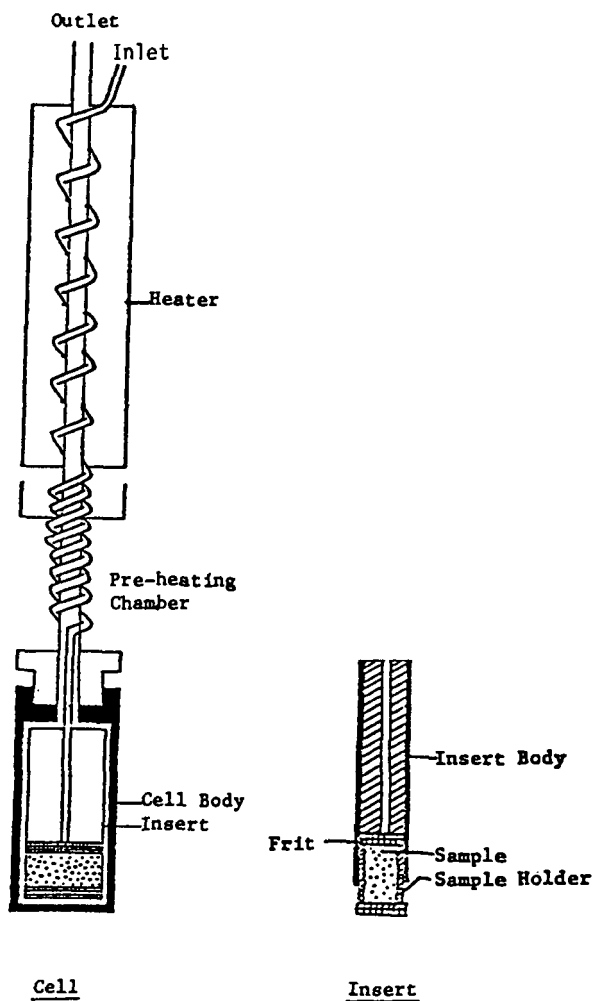
12. Our ΔH_{soln} values for KCl and BaCl₂ of $4.25 \pm 0.0.4$ at 25°C and -6.85 ± 0.30 kcal mole⁻¹ at 75°C agree well with the literature values of 4.20 and -6.76 kcal mole⁻¹ respectively (Gunn, S. J. Phys. Chem. 1965, 69, 2902 and Criss, C. M.; Cobble, J. W. J. Amer. Chem. Soc. 1961, 83, 3223).
13. Our ΔH_{imm} value of -12.55 cal g⁻¹ for Silica gel in water agree with the range of values -11.95 to -13.14 cal g⁻¹ obtained at Bartlesville Laboratory (Noll, L. A. private communication) using different samples of silica gel (Fisher, grade 62).
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18. P_c (isopropylamine) is an average value from estimates using Riedel's and Lydersen's methods reported in ref. 17.

Figure 1. Schematic of Adsorption Flow Calorimeter



- | | |
|--|---|
| 1. Perkin Elmer Model 601
Dual Piston Pumps | 7. Butech Pressure Systems High
Temperature Valve |
| 2. Perkin Elmer Bourden
Pressure Gauges | 8. Valco Filter |
| 3. High Pressure Equipment Co.
Check Valve | 9. Pilgrim Instruments Bourden
Pressure Gauge |
| 4. High Pressure Equipment Co.
Safety Valve | 10,11. Tescom Back Pressure Regulators,
Model 26-1724-24 |
| 5. High Pressure Cell | |
| 6. C-80 Setaram Calorimeter | |

Figure 2. Detail of Adsorption Cell (5 in Figure 1) Showing Preheater Coil



SUPERCRITICAL FLUID ADSORPTION AT THE GAS-SOLID INTERFACE

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INTRODUCTION

Supercritical fluids (SCF) in tandem with adsorbent media are currently being used in a number of chemical processes. Such applications as the regeneration of adsorbents, catalysis under supercritical conditions, analytical and preparative chromatography, and the proposed storage of radioactive gases in their supercritical state (1-4) require an understanding of the role of SCF at the sorbent/gas interface. Adsorbate equilibrium between a dense gas and adsorbent is not totally controlled by the "volatility enhancement" of the sorbate by the supercritical fluid, but can include such additional mechanisms as displacement of the sorbate from the interface by the SCF as well as thermally-induced desorption (5). Unfortunately, many investigators do not appreciate the competitive adsorption effect of the SCF at the gas-solid interface and employ extraction conditions which are solely based on the solubility of the adsorbate in the supercritical fluid. In this presentation, we shall discuss the adsorption of supercritical fluids on active adsorbents and show the relevance of this information for the design of adsorbent regeneration processes.

The physical conditions for regenerating adsorbents vary widely as shown by the reduced state correlation in Figure 1. The choice of these regeneration conditions is partially empirical or based on solute solubilities in the SCF. Whereas, high reduced temperatures (T_r) and pressures (p_r) maybe required to displace polar species or higher molecular weight components from the carbon surface, these conditions can have an adverse effect on the cycle lifetime of the adsorbent. The displacement capability of supercritical fluids on previously adsorbed solutes can be maximized by studying the adsorption isotherm of the SCF on the adsorbent of interest. The results presented in this paper are relevant to the latter phenomena and can be of significant importance in regenerating weak to moderately adsorbed species from the solid surface using minimal gas compression.

EXPERIMENTAL AND DATA SOURCES

Data for the adsorption of supercritical gases on activated carbon were taken from the studies of Ozawa and Ogino (6-8). Correlation of the adsorption maxima for supercritical fluids on various adsorbents as a function of pressure were derived from the work of Menon (9). Tracer pulse chromatographic experiments were performed by the author at the University of Utah. The basic apparatus required for performing these experiments has been previously described (10). Desorption breakthrough volumes were determined at 40°C using supercritical CO₂ and He as carrier gases. Two sorbent columns packed with alumina and crosslinked styrene/divinylbenzene resin were utilized in these studies. Retention volume data were determined for a homologous series of n-alkanes (n-propane through n-heptane) as well as benzene and naphthalene on the above adsorbents.

RESULTS AND DISCUSSION

A typical adsorption isotherm for a supercritical gas adsorbing on activated carbon is shown in Figure 2. Such isotherms show a linear increase in the amount of gas adsorbed with increasing pressure and eventually exhibit a maxima in the pressure range corresponding to $p_r = 0.5-1.0$. The shape of such isotherms is partially influenced by the adsorption and pressure scales that are utilized (11), the maxima being more pronounced when the surface excess is used as a measure of the quantity

of gas adsorbed. Further compression of the SCF results in a decrease of the surface excess as the density of the bulk fluid becomes equal to or exceeds the density of the adsorbed gas. The occurrence of a pressure maximum in the adsorption isotherm for the supercritical gas on a given adsorbent is important, since it represents a condition favorable for the displacement of the adsorbed specie from the adsorbent surface. Typical conditions associated with the occurrence of the pressure maximum (p_{\max}) are presented in Figure 3 for microporous carbons. Note that the pressure requirements for attaining p_{\max} are lower when the adsorption is conducted close to the critical temperature of the gas. This is consistent with the larger uptake of supercritical fluid by the porous medium.

Menon (11) has correlated p_{\max} for various gases in terms of their respective critical properties and has proposed the following equation which is applicable for adsorption on macroporous adsorbents:

$$p_{\max} = p_c T_r^2 \quad 1)$$

The predicted p_{\max} from this relationship have been plotted in Figure 4 from 20 to 100°C for carbon dioxide, ethylene, and chlorotrifluoromethane. The values for p_{\max} obtained from Equation 1 occur at reduced temperatures which are greater than unity, a result which is quite different from the cases cited in Figure 3 for the microporous sorbents.

Studies by several investigators (6-8) utilizing different adsorbent/gas combinations indicate that the pore structure of the adsorbent has a pronounced effect on the value for p_{\max} . As shown in Figure 5, a decrease in the mean pore diameter of the activated carbon decreases the pressure to attain maximum adsorption of the gas. This suggests that there may be some advantage to utilizing a microporous adsorbent in a supercritical fluid regeneration process, provided there is no inhibition to desorption due to restricted diffusion of the displaced adsorbate from the sorbent bed. For activated carbons, the p_{\max} occurs between 25-72 atmospheres depending on the pore size distribution of the adsorbent. Prediction of the adsorption isotherm for the supercritical gas on activated carbons of varying pore size distribution can be accomplished by application of the Pickett equation (6).

The temperature dependence for p_{\max} on carbons exhibiting microporosity is similar to that predicted by Equation 1, however the absolute values for p_{\max} are correspondingly lower due to the pore size dependence. Figure 6 suggests that lower values for p_{\max} can be obtained by reducing both the temperature and pore size of the adsorbent. However, a corresponding reduction in adsorbent surface area occurs upon decreasing the pore size and this is usually undesirable in terms of providing a large adsorbent capacity.

A knowledge of the dependence of adsorbate breakthrough volume on pressure can greatly aid in the design of a supercritical fluid regeneration process. There is a paucity of information in the literature concerning this phenomena, hence, we have measured the desorption breakthrough volumes for reversibly adsorbed species on beds of alumina and crosslinked styrene/divinylbenzene resin using the elution pulse analog of frontal analysis. The desorption breakthrough volume, V_b , can be readily obtained from the capacity factor, k' , for the various injected sorbates and is given by Equation 2 as:

$$V_r = V_0 (k' + 1) \quad 2)$$

where V_0 is the void volume of the column.

Figure 7 illustrates the dependence of the desorption breakthrough volume on gas pressure for benzene desorbing from crosslinked resin matrix. Close examination of the plot reveals that there is a linear decrease in the breakthrough volume for benzene up to a pressure of approximately 70 atmospheres. Beyond this pressure, there is a rather dramatic decrease in breakthrough volume which continues up to a pressure of 100 atmospheres. Benzene breakthrough volumes at pressures beyond 100

atmospheres tend to asymptotically approach a constant volume largely determined by the dimensions associated with the bed voidage. This general trend in desorption breakthrough behavior has been confirmed by running additional solutes on both alumina as well as the crosslinked resin. Interestingly, the transition to a constant breakthrough volume occurs in approximately the same pressure range for all of the adsorbates we have studied suggesting the maximum adsorption of the carrier fluid occurs in this pressure interval. This result suggests that carbon dioxide is displacing the adsorbate from the surface of the adsorbent. It should be noted, that selective fractionation of the adsorbed solutes can be achieved by operating in the lower pressure regime, but this segregation capability is rapidly lost when pressures exceed 80 atmospheres.

The above behavior has been verified with similar adsorbates on alumina columns. Figure 8 shows the dependence of the capacity factor for n-butane adsorbing on alumina as a function of gas pressure. The recorded decrease in the capacity factor parallels the reduction in adsorbate breakthrough volume as a function of pressure and it becomes constant as the breakthrough volume approaches the void volume of the adsorbent bed. Additional experiments performed using helium as a carrier gas also showed a decrease in the k' for n-butane as a function of increasing gas pressure. As shown in Figure 8, the magnitude of this change was not as dramatic as that exhibited for the alumina- CO_2 -n-butane system, however the recorded reduction in k' suggest that a displacement mechanism is responsible for the capacity factor changes when using this relative inert gas.

The above results strongly support the hypothesis that displacement of bound adsorbates by a supercritical fluid can be a major factor in regenerating adsorbent beds. Additional support for this concept can be found from the regeneration studies of Eppig and coworkers (3) who recovered ethanol, methyl ethyl ketone, and toluene from activated carbon beds using modest CO_2 pressures (100 atm.). Competitive adsorption studies of CO_2 /light hydrocarbon mixtures desorbing from molecular sieves (12) also indicate that CO_2 is preferentially adsorbed over the alkane moieties. Clearly, this mode of adsorbent regeneration can be used for desorbing selected solutes without the need for excessive gas compression.

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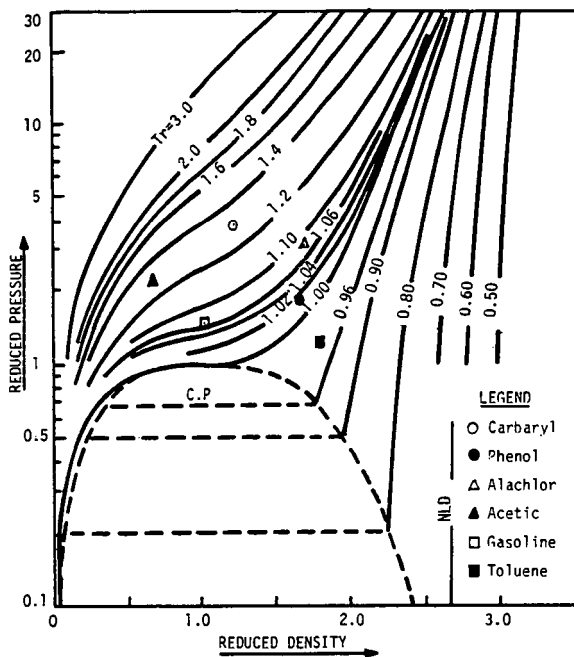


FIGURE 1. Reported Conditions for SCF Desorption of Selected Adsorbates from Activated Carbon

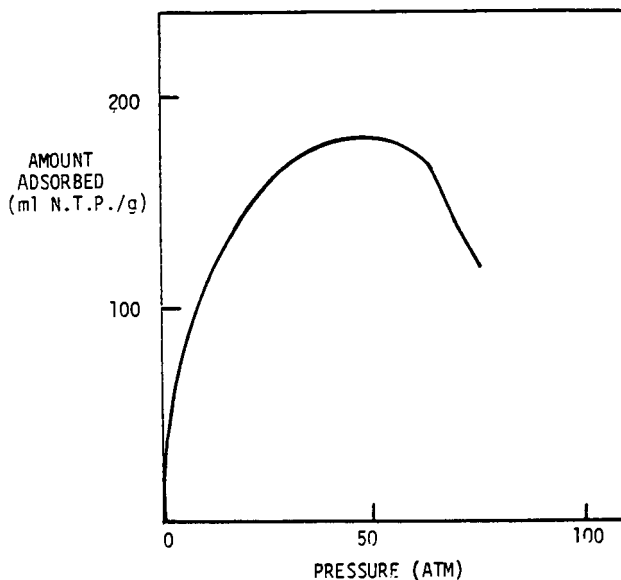


FIGURE 2. Adsorption Isotherm for the CO_2 /Activated Carbon System

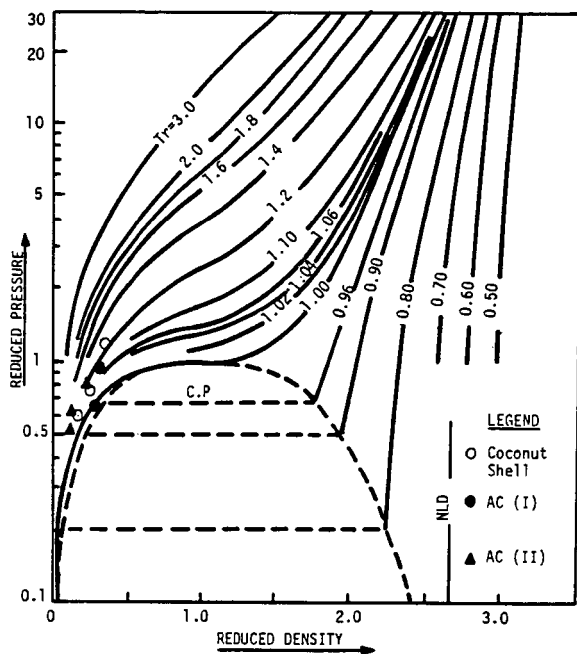


FIGURE 3. Conditions for Occurrence of Adsorption Maximum (P_{\max}) in CO_2 /Activated Carbon Systems

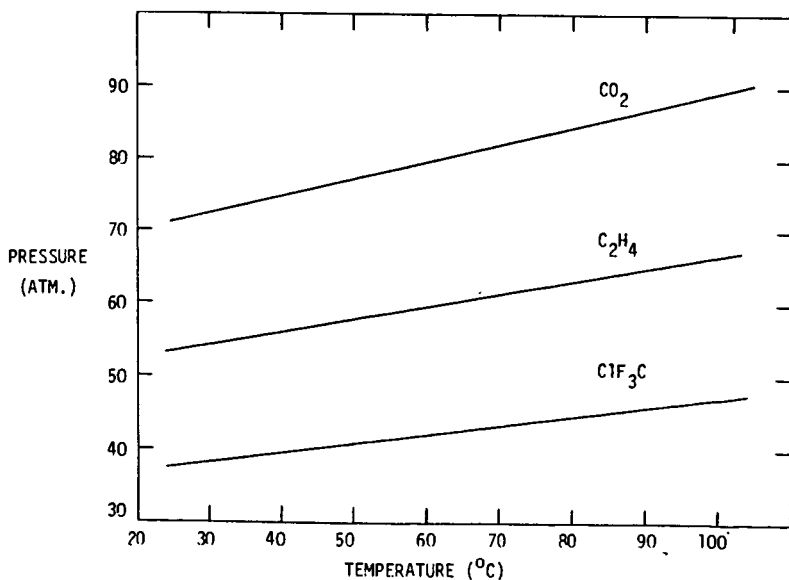


FIGURE 4. Dependence of P_{\max} on Temperature According to Menon for Various Gases

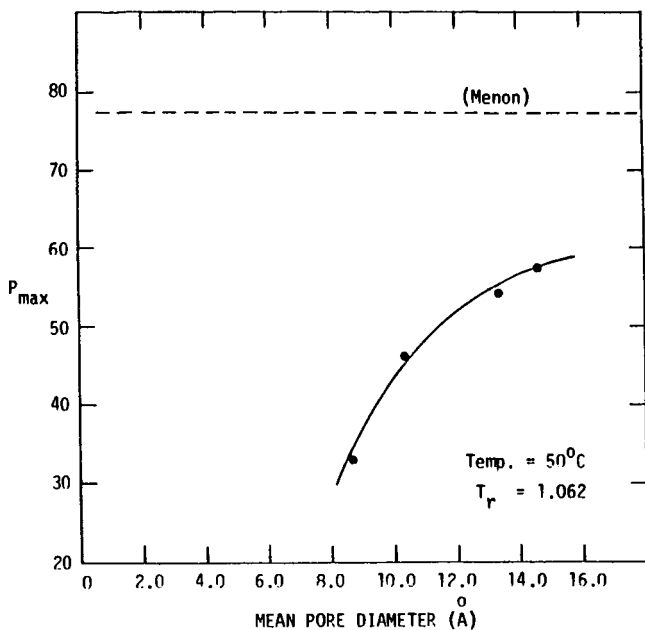


FIGURE 5. Pressure For Maximum Gas Adsorption vs. Mean Pore Diameter of Activated Carbons

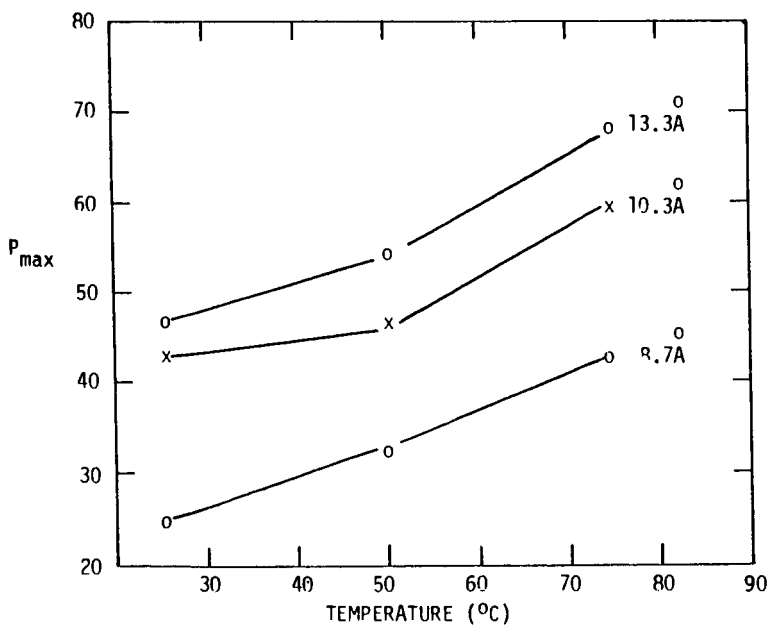


FIGURE 6. P_{\max} vs. Temperature for CO_2 Adsorption on Activated Carbons of Various Pore Sizes

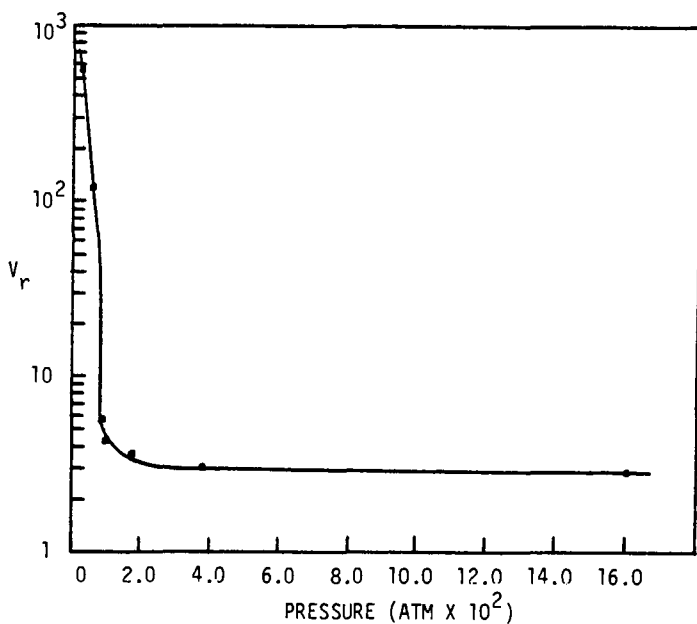


FIGURE 7. Desorption Volume (V_r) vs. CO_2 Pressure for Benzene/Styrene-Divinylbenzene Resin System

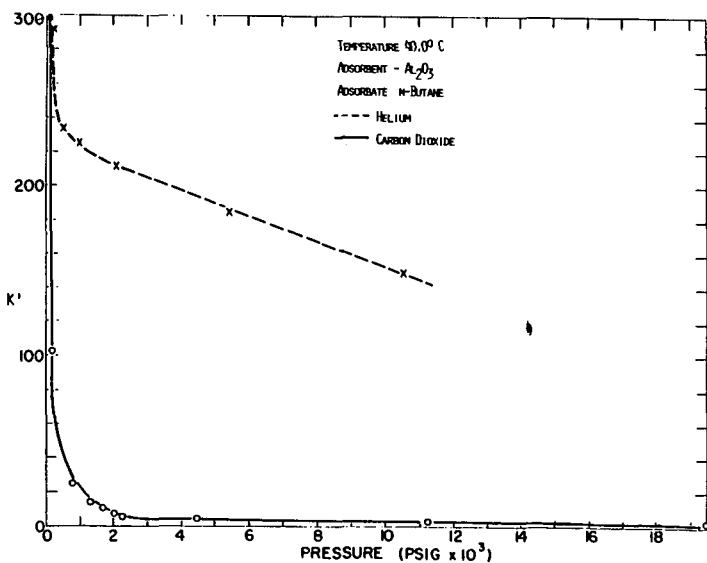


FIGURE 8. Capacity Factor (k') for n-Butane on Al_2O_3 vs. Carbon Dioxide or Helium Pressure

SOLUBILITIES OF SOLID n-ALKANES IN SUPERCRITICAL ETHANE

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ABSTRACT

The solubilities of solid n-triacontane ($n\text{-C}_{30}\text{H}_{62}$) and n-dotriacontane ($n\text{-C}_{32}\text{H}_{66}$) in supercritical ethane at temperatures between 308K and 319K and pressures upto 20 MPa are reported in this work. The results have been correlated using an equation of state, using sublimation pressures which are extrapolated from data available for the lower even-numbered members of the alkane series.

INTRODUCTION

Then n-alkanes are an interesting series because they display great regularity in their behavior. Many of their fluid phase properties, for example, can be correlated with the number of carbon atoms in the molecules. In order to develop general relations for supercritical extraction, therefore we have studied the solubilities of solid n-alkanes in supercritical ethane. The solubilities of n-triacontane ($n\text{-C}_{30}\text{H}_{62}$) and n-dotriacontane ($n\text{-C}_{32}\text{H}_{66}$) in ethane are reported in this paper. Results for n-tetracosane ($n\text{-C}_{24}\text{H}_{50}$), n-hexacosane ($n\text{-C}_{26}\text{H}_{54}$) and n-octacosane ($n\text{-C}_{28}\text{H}_{58}$) will also be presented at the symposium. One reason for studying only the even-numbered members of the n-alkane series is that they exhibit different packing properties than the odd-numbered members of the series [1,2,3]. Thus their solid phase properties such as heats of sublimation and vapor pressures follow different trends from those of the odd-numbered members. This is shown in Fig. 1 for the heats of sublimation. Any generalizations for supercritical extraction of solids must therefore take account of this difference in behavior.

EXPERIMENTAL

The apparatus used in this study was a single-pass flow system shown

schematically in Fig. 2. The apparatus is similar in principle to those used by Kurnik et al [4] and others [5,6,7]. Solvent gas is first liquefied and then compressed past its critical pressure by means of a Milton Roy minipump A. Its temperature is increased to supercritical conditions in the heat exchange coil B immersed in a constant-temperature water bath C. The bath temperature was maintained constant to $\pm 0.1\text{K}$ and the temperature monitored by means of a copper-constantan thermocouple D calibrated against an NBS-certified platinum resistance thermometer. The pressure of the system was measured by a Heise gauge E calibrated against a dead-weight gauge. The pressure was maintained constant by a back pressure regulator F. The supercritical solvent was then brought into contact with the solute in a modified Jerguson equilibrium cell G. The equilibrium temperature was measured by a second copper-constantan thermocouple K calibrated against an NBS-certified platinum resistance thermometer. This thermocouple was inserted inside the cell by means of a fitting. For better solid contact, layers of glass beads were packed with the solute in the equilibrium cell. The loaded supercritical fluid was then depressurized at the micrometering valve H and the deposited solute was collected in a separation vessel J. The micrometering valve was heated to compensate for the Joule-Thompson effect upon depressurization and all the lines outside the constant temperature bath were heat traced. In spite of these precautions, however, some of the long-chain n-alkanes still precipitated inside the micrometering valve. This deposited solid was flushed out with liquid hexane at the end of each run. The solute collected was weighted to $\pm 0.10\text{ mg}$ using a Mettler electronic balance. Solvent volume was recorded using a wet test meter L. We estimate the precision of our temperature, pressure and volume measurements to be 0.5 K, 0.5 mmHg and $\pm 1/2\%$ respectively; the accuracies were typically twice the magnitude of the precision.

RESULTS

For comparison purposes, the solubilities of 2,3-dimethylnaphthalene in CO_2 along three isotherms were first measured and the results compared with those of Kurnik et al [4]. These results are presented in table 1 for the 308.15K isotherm. In no case did our solubilities differ from those of Kurnik et al by more than 3.6% for any of the isotherms.

Our results for the $C_2H_6 + n C_{30}H_{62}$ and $C_2H_6 + n C_{32}H_{66}$ systems are shown in Tables 2 and 3. Since the sublimation pressures of the higher n-alkanes were not available in the literature, we have treated these as adjustable parameters in our equation of state correlations of the solubility data. The sublimation pressures were not freely adjustable, however, but were bounded by the values obtained by extrapolating propane and n-octadecane sublimation pressures 25%. Our results are shown in Fig 3 and 4. Additional results will be discussed at the symposium. The equation of state used was that of Patel and Teja [8].

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TABLE I

Comparison of $\text{CO}_2 + 2,3$ Dimethylnaphthalene
Data at 308.15K

System Pressure MPa	$Y_{2,3\text{-DMN}} \times 10^3$	
	This Work	Kurnik et al
9.87	2.28	2.2
14.25	4.36	4.41
19.60	5.45	5.42
24.12	5.76	5.82
27.92	6.45	6.43

TABLE II

Results for Ethane-n-Triacontane ($\text{C}_{30}\text{H}_{62}$)

System Pressure MPa	$Y_{\text{C}_{30}\text{H}_{62}} \times 10^3$	
	308.15K	313.15K
6.57	0.549	0.486
10.10	1.24	1.95
13.64	1.71	3.50
16.67	2.24	
20.20	3.20	

TABLE III

Results for Ethane-n-Dotriacontane ($\text{C}_{32}\text{H}_{66}$)

System Pressure MPa	$Y_{\text{C}_{32}\text{H}_{66}} \times 10^3$		
	308.15K	313.15K	319.15K
6.57	0.216	0.177	0.149
10.10	0.713	0.953	1.28
13.64	0.958	1.44	2.14
16.67	1.26	1.73	
20.20	1.81	2.18	

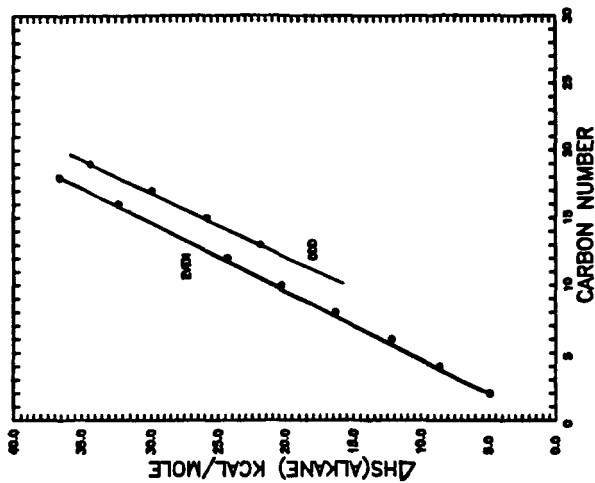


Figure 1. Heat of Sublimation vs. Carbon Number

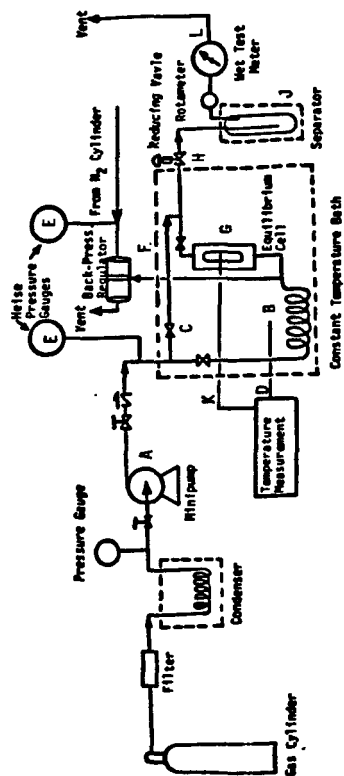


Figure 2. Supercritical Flow Apparatus

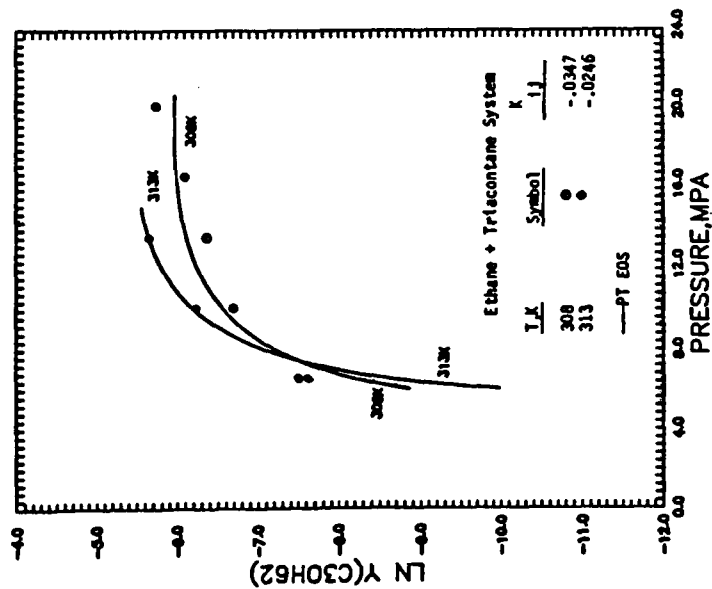


Figure 3. Solubility of Triacontane in Supercritical Ethane

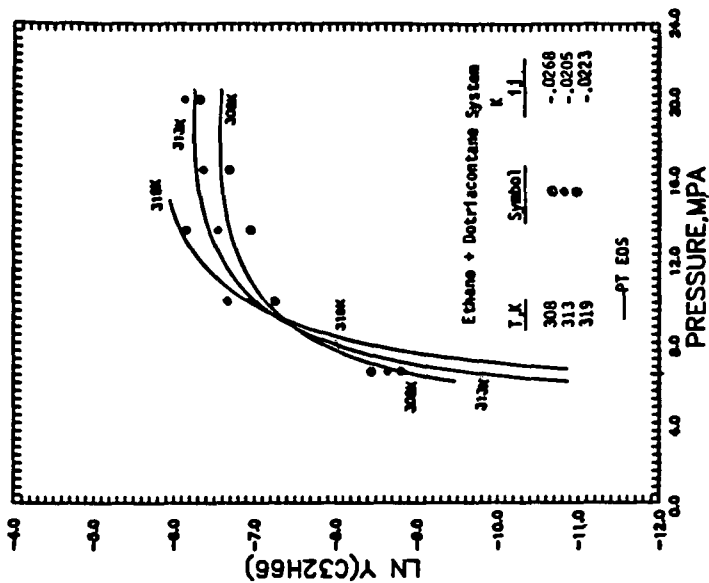


Figure 4. Solubility of Dotriacontane in Supercritical Ethane

High-Pressure Phase Equilibria in Ternary Fluid Mixtures with a Supercritical Component

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The potential of supercritical extraction (SCE), a separation process in which a gas above its critical temperature is used as a solvent, has been widely recognized in the recent years. The first proposed applications have involved mainly compounds of low volatility, and processes that utilize supercritical fluids for the separation of solids from natural matrices (such as caffeine from coffee beans) are already in industrial operation. The use of supercritical fluids for the separation of liquid mixtures, although of wider applicability, has been less well studied, as the minimum number of components for any such separation is three (the solvent, and a binary mixture of components to be separated). The experimental study of phase equilibrium in ternary mixtures at high pressures is rather complicated, and theoretical methods to correlate the observed phase behavior are lacking.

One important potential application of supercritical extraction is in the recovery of polar organic compounds from aqueous solutions. Such mixtures arise very frequently as products of biochemical syntheses. In many cases, the costs of the energy-intensive separations are quite high. It is the objective of an ongoing research project at MIT to investigate the applicability of SCE for such separations.

Previous work in the area of high-pressure phase equilibrium of aqueous solutions of organic compounds with supercritical fluids includes the pioneering work of Elgin and Weinstock (1) carried out in the 1950's. Francis (9) presented a large number of qualitative results for ternary systems of liquid CO₂ at 25 °C. In the more recent years, Paulaitis et al. (2,3), Kuk and Montagna (4), McHugh et al. (5) and Radosz (6) have reported measurements in systems with some of the first alcohols, water and supercritical fluids.

Experimental

The experimental setup that is being used is shown in Figure 1. The main element of the equipment is a visual high pressure cell (Jerguson gage model 19-TCH-40) with an internal volume of about 50 cm³, that serves as a mixing and separating vessel, as well as for the visual observation of the number and quality of the coexisting phases. Connections at the bottom, top and side of the vessel permit withdrawal of the lower, upper and middle phases, any two of which can be recirculated externally with a dual high pressure Milton-Roy Mini Pump. An on-line Mettler-Paar vibrating tube density meter (DMA 60 with a DMA 512 cell) is used to measure the density of one of the recirculating phases at a time, and can be switched between any of them.

The Jerguson gage is immersed in a constant temperature bath with silicon fluid as the heat-transfer medium, that also thermostats the density meter. The bath temperature is controlled to $\pm .01$ K with a Thermomix 1460 temperature regulator, and the temperature is measured with a calibrated mercury-in-glass thermometer to within .01 K. The lines external to the bath are maintained at the bath temperature with the help of heating tapes, and the temperature at several points is monitored with thermocouples. Pressure is measured with two calibrated Heise pressure indicators to within $\pm .16$ bar for pressures up to 160 bar, and to within $\pm .4$ bar for pressures up to 350 bar.

Sampling is done with two high pressure-switching valves of internal volume .5 μ l (for the upper phase) and .2 μ l (for the lower or middle phases). The samples are directly depressurized into a He carrier gas stream and analyzed with a Perkin Elmer Sigma 2 Gas Chromatograph, using a Porapak Q column supplied by Supelco. The response factors for the materials used were found to be close to those reported by Dietz (7). Typical reproducibility of the analysis is $\pm .003$ in mole fraction, with somewhat larger deviations for the gas-phase composition at low pressures.

After purging and evacuation of the equipment the cell is charged with a liquid mixture of known composition and with the supercritical component up to the desired pressure. The recirculation pumps are started, and the approach to equilibrium monitored by the stability of the pressure, density, and composition measurements with time. For the mixtures studied, a typical equilibration time is 15 min., but at least 30 min are allowed before the final sampling. At least two samples are taken from each phase at equilibrium. A new pressure point can then be established immediately by introducing or removing supercritical fluid and/or liquid, so that the level of the interfaces in the cell at the new desired pressure is appropriate for sampling through the available ports.

Results

Binary Systems

As a test of the validity of the equipment design and the experimental procedures, we first investigated a binary system for which results have been previously published. Knowledge of the behavior of the binary systems is in itself important, since the data provide the appropriate limits for the corresponding ternary systems.

In Figure 2 we present the experimental results and literature data for the system CO_2 - acetone at 313 and 333 K (literature results are available only at the lower temperature). As can be seen, the agreement between the two sets of results is excellent. Also shown on the same figure as continuous lines are the results of the fitting of the experimental data using a modified Peng-Robinson equation of state that is described in the Appendix. The agreement between experimental and predicted phase compositions is within the experimental uncertainty of the data, except in the critical region.

Several of the features of the phase behavior shown on Figure 2 are quite general. In particular, it can be seen that the solubility of CO_2 in the liquid phase is quite high, even at moderate pressures. The system critical pressure is, in general, comparable to the critical pressure of CO_2 , and increases with temperature at the temperature range studied. Although the solubility of acetone in the gas phase is low in the two-phase region, there is complete miscibility between CO_2 and acetone at pressures that are not very high. CO_2 at liquid-like densities is an excellent solvent for a wide range of organic compounds, as was first observed by Francis (9) for near critical liquid CO_2 .

One additional example of the same general type of behavior is demonstrated by the CO_2 - ethanol system. Three measured isotherms for this system are presented in Figure 3. No comparable set of experimental results appears to be available in the open literature. Again, the agreement between experimental results and model predictions is very good.

Ternary Systems

As one of a series of model systems, we studied the CO_2 - acetone - water system at 313 and 333 K. The most striking feature of the system behavior, is a very extensive three-phase region at both temperatures. The three-phase region is first observed at a pressure of only 25 bar at 313 K, and extends to approximately the critical pressure of the binary CO_2 - acetone system. Table 1 provides the experimental results for the composition of the three phases at equilibrium as a function of pressure and temperature.

The physical picture that underlies this behavior, as pointed out first by Elgin and Weinstock (1), is the 'salting out' effect by a supercritical fluid on an aqueous solution of an organic compound. As pressure is increased the tendency of the supercritical fluid to solubilize in the organic liquid results in a phase split in the aqueous phase, at what can be named a lower critical solution pressure (which varies with temperature). As pressure

is further decreased, the second liquid phase and the supercritical phase become more and more similar to each other, and merge at an upper critical solution pressure, above which only two phases can coexist.

This pattern of behavior was also observed by Elgin and Weinstock for the system ethylene - acetone - water at 15 °C. In addition, the same type of behavior, but at quite different pressures relative to the pure solvent critical pressure was reported by Paulaitis et al.(3) for the system CO₂ - isopropanol - water, by McHugh et al.(5) for the system ethane - ethanol - water and again by Paulaitis et al.(2) for the CO₂ - ethanol - water system, and therefore appears to be quite general.

A more complete picture of the phase equilibrium behavior is given in Figure 4 for the system under study at 333 K. The darker lines and squares on this figure are experimentally measured tie-lines and phase compositions. The light lines are model predictions, using values of interaction parameters determined solely from regression of binary data (see Appendix). The two sets of results are in good agreement with each other.

An interesting feature of the phase equilibrium behavior is the relative insensitivity of the phase envelope and positions of the tie-lines to variations in pressure in the two-phase region, as evidenced by comparison of the diagrams at 100 and 150 bar in Figure 4. This would seem to imply that similar separations can be achieved by operation at pressures just above the upper critical solution pressure of ~95 bar as compared to operation at higher pressures.

The phase equilibrium behavior at 313 K is quite similar to that at 333 K, with the three-phase region shifted to lower pressures, as presented in Table 1.

From an engineering point of view, the most important quantities in the evaluation of a separation scheme based on a phase behavior pattern such as the one shown, are the selectivity of the separation with respect to the desired component, as well as the loading of the desired component in the extractant phase. It is well known that those two factors usually increase in different directions. Figures 5 and 6 present experimental data and model predictions for the distribution coefficient of acetone, and for the selectivity ratio α of acetone over water (defined as the ratio of distribution coefficients of acetone and water in the liquid and fluid phases), as a function of the water concentration in the liquid phase. The distribution factor shows a sharp maximum at both temperatures, with a higher value at the higher temperature, whereas the selectivity decreases smoothly from the limiting value of ~300 at low acetone concentrations to 1 as the plait point is approached. The experimental data show the same trends, although there is some scatter that is due to the fact that small absolute errors in the low supercritical phase concentrations of acetone and water result in large relative errors for the distribution coefficient and selectivity factors. Selectivities are generally higher for the lower temperature, but loadings are lower. Based on the observed behavior for the system, the maximum CO₂-free acetone concentrations in the upper phase is 85% mole (~95% w/w) acetone for operation at 150 bar and 333 K.

Conclusions

An apparatus for the determination of high pressure phase equilibrium data for mixtures of water, polar organic liquids and supercritical fluids was constructed and successfully operated for binary and ternary systems with supercritical carbon dioxide.

The system CO₂ - acetone - water was extensively investigated at 313 and 333 K. The system demonstrates several of the general characteristics of phase equilibrium behavior observed earlier for similar systems, including an extensive LLV region that appears at relatively low pressures.

A model based on a modified form of the Peng-Robinson equation of state was able to reproduce quantitatively all features of the observed phase equilibrium behavior, with model parameters determined from only binary data. The use of such models may facilitate substantially the task of process design and optimization for separations that utilize supercritical fluids.

A substantial sensitivity of the separation efficiency, as determined by the ability of the solvent to selectively extract the organic compound with high loadings was observed when the operating conditions were varied.

Acknowledgement

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APPENDIX

Equation of State used

For the correlation of the experimental results, we used a modification of the Peng-Robinson equation of state developed by the authors. The essence of the method, which is presented in detail in (8), is the use of a non-quadratic mixing rule for the attractive parameter a , that involves two binary interaction parameters. The equations for the pressure, the mixing rule used and the resulting expression for the chemical potential of a component in a mixture are shown below.

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V^2 + uVb_m + wb_m^2} \quad 1)$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad 2)$$

$$b_m = \sum_i x_i b_i \quad 3)$$

$$a_{ij} = \sqrt{a_i a_j} [1 - k_{ij} + (k_{ij} - k_{ji})x_i] \quad 4)$$

$$\begin{aligned} \ln \phi_k = \ln \frac{\hat{f}_k}{x_k P} = & \frac{b_k}{b_m} \left(\frac{PV}{RT} - 1 \right) - \ln \frac{P(V-b)}{RT} + \\ & + \left[\frac{\sum_i x_i (a_{ik} + a_{ki}) - \sum_i \sum_j x_i^2 x_j (k_{ij} - k_{ji}) \sqrt{a_i a_j} + x_k \sum_i x_i (k_{ki} - k_{ik}) \sqrt{a_k a_i}}{a_m} - \frac{b_k}{b_m} \right] \times \\ & \times \frac{a_m}{\sqrt{u^2 - 4w} b_m RT} \ln \frac{2V + b_m (u - \sqrt{u^2 - 4w})}{2V + b_m (u + \sqrt{u^2 - 4w})} \quad 5) \end{aligned}$$

For the estimation of the subcritical pure component parameters, we used the technique of Panagiotopoulos and Kumar (11), that provides results that exactly reproduce the vapor pressure and liquid density of a subcritical component. Table 2 presents the pure component parameters that were used. For the supercritical components, the usual acentric factor correlation was utilized.

It is important to note, that the interaction parameters between the components (two per binary) were estimated solely from binary phase equilibrium data (including low-pressure VLE data for the binary acetone - water); no ternary data were used in the fitting. The values of the interaction parameters obtained are shown in Table 3.

TABLE 1 : Three phase equilibrium compositions for the system Water (1) - Acetone (2) - CO₂ (3)

P (bar)	lower phase		upper phase		middle phase	
	x ₁	x ₂	y ₁	y ₂	z ₁	z ₂
T = 313 K						
29.3	0.810	0.153	0.005	0.025	0.294	0.454
35.9	0.864	0.106	0.006	0.019	0.197	0.427
43.2	0.904	0.075	0.003	0.017	0.153	0.360
55.9	0.920	0.052	0.002	0.015	0.119	0.230
61.1	0.942	0.037	0.004	0.015	0.114	0.191
65.8	0.944	0.032	0.002	0.015	0.130	0.148
75.2	0.959	0.017	0.002	0.014	0.020	0.069
79.6	0.966	0.011	0.002	0.015	0.049	0.035
T = 333 K						
39.4	0.795	0.163	¹	¹	0.400	0.398
51.1	0.880	0.091	¹	¹	0.182	0.418
59.4	0.906	0.068	0.006	0.030	0.173	0.359
70.3	0.925	0.049	0.008	0.035	0.117	0.300
79.2	0.939	0.039	0.006	0.032	0.089	0.234
92.6	0.946	0.029	0.010	0.046	0.084	0.127

¹ not available

TABLE 2 : Pure component parameters

Component	T(K)	a ($\text{J}\cdot\text{m}^3/\text{mol}$)	10^6 b (m^3/mol)
Acetone	313.15	2.1772	62.35
	333.15	2.1165	62.65
Ethanol	308.15	2.0292	48.23
	323.15	1.9679	48.44
	338.15	1.9069	48.61
Water	313.15	.81614	16.07
	333.15	.79123	15.99

TABLE 3 : Interaction parameters

System	T (K)	k_{12}	k_{21}
CO ₂ (1) - acetone(2)	313.15	-0.02	0.00
	333.15	-0.02	0.00
CO ₂ (1) - ethanol(2)	308.15	0.072	0.069
	323.15	0.093	0.077
	338.15	0.089	0.061
CO ₂ (1) - water(2)	313.15	-0.205	0.162
	333.15	-0.185	0.160
acetone(1) - water(2)	313.15	-0.310	-0.150
	333.15	-0.293	-0.132

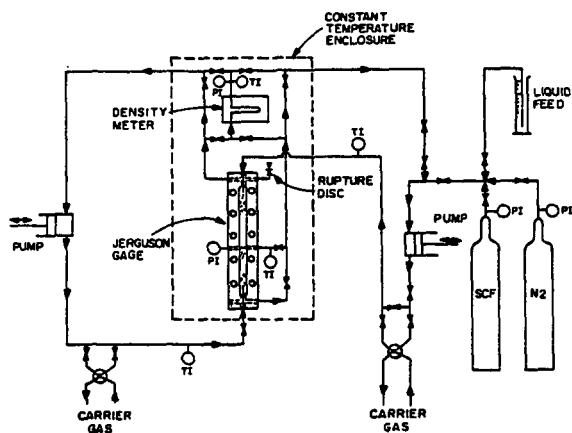


Figure 1 Schematic drawing of the equipment

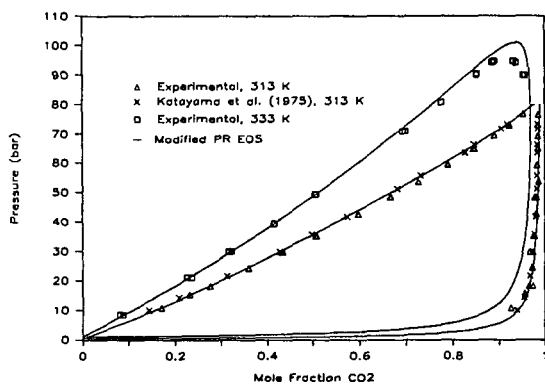


Figure 2 Experimental (crosses), literature (squares) and predicted (lines) phase equilibrium behavior for the system CO₂(1) - Acetone(2) at 313 and 333 K. Experimental data are from reference (10).

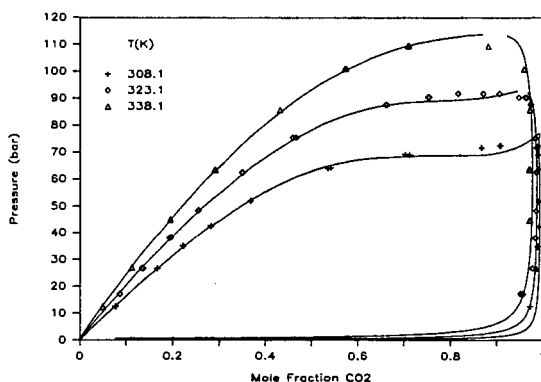


Figure 3 Experimental (symbols) and predicted (lines) phase equilibrium behavior for the system $\text{CO}_2(1)$ - water(2) at 308, 323 and 338 K

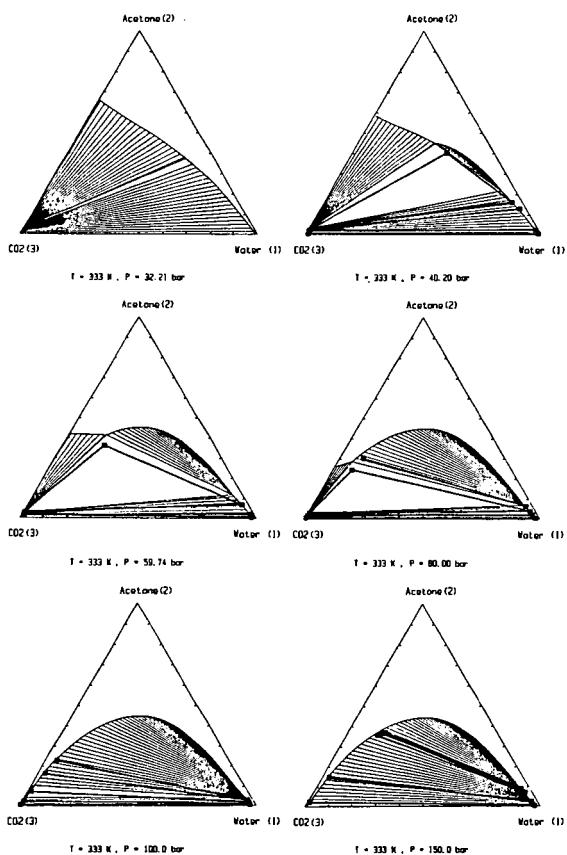


Figure 4 Experimental (dark lines and squares) and predicted (light lines) phase equilibrium behavior for the water(1) - acetone(2) - $\text{CO}_2(3)$ system at 333 K.

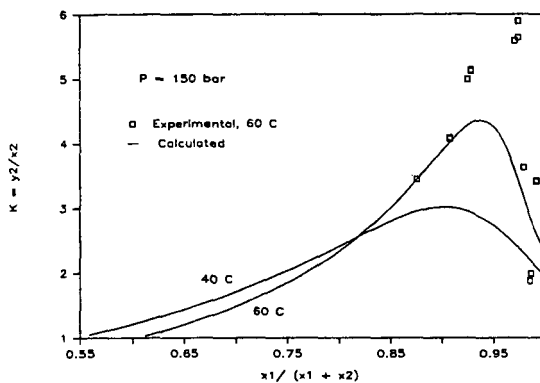


Figure 5 Distribution coefficient for acetone from experimental data (points) and model predictions (lines) for the water(1) - acetone(2) - CO_2 (3) system at 150 bar, as a function of the water concentration in the lower phase (on a CO_2 -free basis).

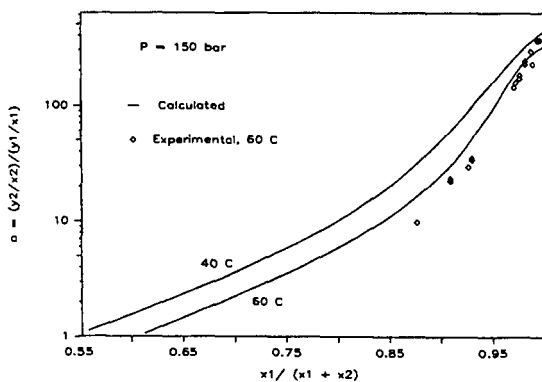


Figure 6 Selectivity factor for acetone over water for the water(1) - acetone(2) - CO_2 (3) system at 150 bar, as a function of the water concentration in the lower phase (on a CO_2 -free basis).

Multiphase Behavior in Ternary Mixtures of Elevated Pressures

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INTRODUCTION

Separations using supercritical or near-critical fluids as solvents are frequently carried out in the presence of water. Extraction of products from fermentation broths, tertiary oil recovery by CO_2 flooding, and supercritical-fluid (SCF) chromatography are examples of separations in which water can be present. Such systems will often exhibit phase behavior in which several coexisting fluid phases are present at equilibrium. For example, extensive regions of liquid-liquid-gas equilibrium have been observed for water-alcohol-SCF mixtures (1-3), and even four coexisting phases (liquid-liquid-liquid-gas) have been observed for n-propanol-water- CO_2 mixtures(4).

There are several practical implications of three-phase, liquid-liquid-gas equilibrium. For conventional extraction processes, it is desirable to avoid such regimes, or in the case of CO_2 flooding of oil reservoirs, to accurately account for multiple phases in determining extraction efficiency. Alternatively, the formation of two liquid phases in the presence of a compressed gas can be exploited to achieve a desired separation.

In this paper, we present the results of an investigation of fluid phase equilibria at elevated pressures for the system isopropanol-water- CO_2 . These results include measured equilibrium compositions for two, three, and four coexisting fluid phases over a range of temperatures and pressures in the vicinity of the critical point of CO_2 . A computer simulation of the phase equilibria for this three-component system is also presented. The simulation, which is based on the Peng-Robinson equation of state(7) and the experimental results, demonstrates the complexity of phase behavior that can be obtained for aqueous solutions in the presence of SCF solvents. This phase behavior must be understood for correct interpretation of SCF extraction experiments, and for design of separation processes using supercritical or near-critical solvents at elevated pressures.

EXPERIMENTAL SECTION

Phase compositions (tie lines) for liquid-gas equilibrium were measured using a flow technique for mixing and for continuous sampling of the phases. Equilibrium compositions for three and four coexisting phases were obtained using a static technique with a variable-volume view cell. This technique

involved calculating phase compositions from component material balances and measured phase volumes at known cell loadings; no sampling of the individual phases is required. Both experimental techniques are described in detail elsewhere(5,6).

Phase compositions for liquid-gas and liquid-liquid-gas equilibria were measured as a function of pressure at several constant temperatures. Figure 1 shows these results for 60°C in the form of triangular phase diagrams corresponding to different pressures. The two-phase regions which bound the three-phase triangles at the intermediate pressures have been omitted for clarity. At lower temperatures, four equilibrium phases were observed, and Figure 2 gives the measured compositions of these phases at 40°C and 1110 psia.

EQUILIBRIUM PHASE BEHAVIOR

The phase behavior depicted in Figure 1 shows a dramatic shift in the tie lines for liquid-gas equilibrium as pressure is changed from 1500 psia to 2000 psia. At the lower pressure, the solubilities of water and isopropanol in supercritical CO₂ are low, although the selectivity for the alcohol is high. At 2000 psia, high solubilities are obtained with lower alcohol selectivities. A continuous shifting of the tie lines between these two pressures can not be obtained, however, as three coexisting phases emerge at intermediate pressures. With increasing pressure, the water-rich liquid phase splits into two liquid phases at a pressure between 1500 and 1600 psia (a critical endpoint). As pressure is increased further, the composition of the liquid phase of intermediate density, L₂, approaches that of the carbon dioxide-rich gas phase, and the alcohol concentration initially increases and then decreases. Eventually the L₂ phase and the gas phase merge to form a single fluid phase (another critical endpoint) at a pressure just below 2000 psia.

One practical implication of this phase behavior is that the solvent properties of CO₂ can be changed significantly over a relatively small pressure range. Thus solvent/extract separation can be easily achieved, and an optimal ratio of solvent capacity to selectivity can potentially be selected, depending on whether three coexisting phases can be avoided in the separation process. It is also possible to use the two liquid phases to separate other components that would be present in dilute aqueous solution by distributing these components between the L₁ and L₂ phases. The advantage of such a separation would include (1) moderate operating temperatures and pressures, (2) the ability to control the composition of the intermediate phase with pressure, (3) the complete reversibility of the phase splitting, and (4) the ability to form two liquid phases with components that are similar in molecular nature.

The four-phase equilibrium illustrated in Figure 2 suggests that the phase behavior for this ternary mixture can be quite complex at conditions near the critical point of CO₂. In order to describe global phase equilibria for this system, the Peng-Robinson equation of state was fit to the

experimental results and then used to predict phase behavior over an extended region of temperatures and pressures. Details of these calculations are given elsewhere(6). The calculated pressure-temperature projection for isopropanol-water-CO₂ is given in Figure 3. This projection depicts the four-phase (LLLG) line for the ternary mixture, the three-phase (LLG) line for the binary water-CO₂ system, the vapor pressure curve for carbon dioxide (CO₂ VP), and the liquid-gas and liquid-liquid critical lines (dashed lines) which bound the three-phase regions for the ternary mixture.

Two important aspects of the phase behavior are evident from this projection. First, the three-phase region extends to relatively high temperatures and pressures; that is, the multiphase behavior is not limited to conditions close to the critical point of CO₂. Second, at temperatures and pressures near this critical point, the phase behavior can be quite complex. Four different three-phase regions bound the four-phase line, and there are five different two-phase regions which bound these three-phase regions. Obviously, simple screening experiments on this three-component system to obtain "representative" alcohol/water solubilities in compressed CO₂ could give dramatically different results depending on the temperature, pressure, and mixture composition examined. At temperatures below 20°C, even more complex behavior is possible since a solid hydrate phase can also be obtained.

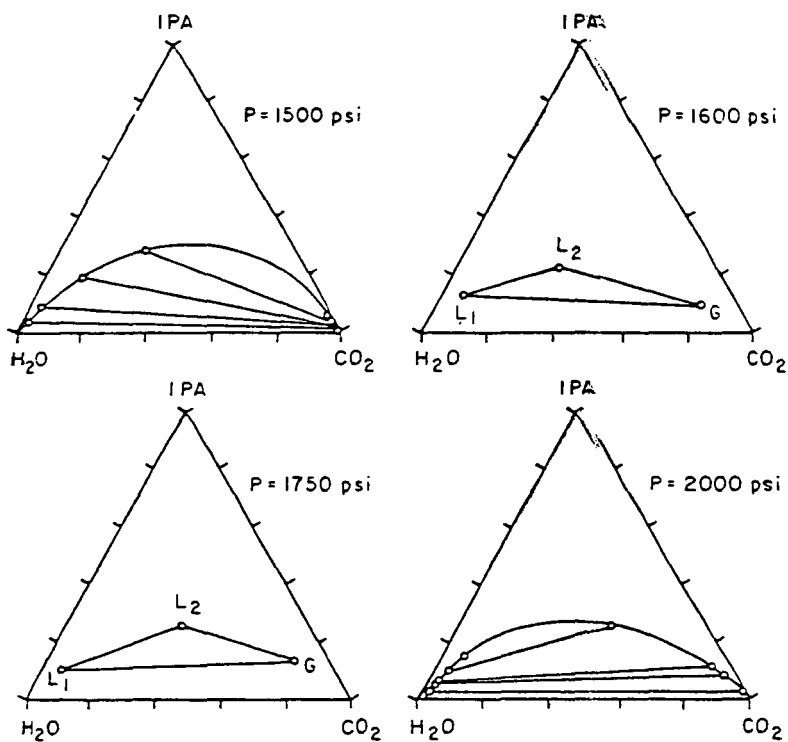
In conclusion, our experimental results and model calculations demonstrate that complex multiphase behavior can occur for mixtures containing water and supercritical or near-critical fluids at elevated pressures. The ability to predict such behavior is an important factor in interpreting solubility behavior for SCF solvent extractions and for the design of separation processes using dense fluids at elevated pressures. The ability to form two liquid phases in the presence of a compressed gas can also be exploited to achieve a desired separation of nonvolatile components in dilute aqueous solutions where it is not possible to dissolve these components in a dense fluid such as compressed CO₂.

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FIGURE 1.

Experimental Two-Phase
and Three-Phase Equilibria at 60°C



Two-Phase Data of Kander, 1984

Figure 2.

Experimental Four-Phase Compositions
at 40°C and 1110 psi

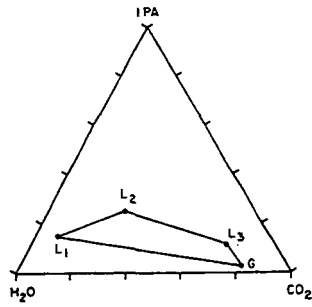


Figure 3.

Model Generated Pressure-Temperature Projection
for Isopropanol-Water-Carbon Dioxide

